DETAILED STUDY OF THE REACTION MECHANISM OF SPONTANEOUS COMBUSTION OF COAL WITH PARTICULAR EMPHASIS ON WESTERN CANADIAN LOW-RANK COALS

A REPORT BY

AMITABHA MAJUMDAR and FRANK W. BACHELOR

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF CALGARY

CALGARY, ALBERTA

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THE UNIVERSITY OF CALGARY

2500 University Drive N.W., Calgary, Alberta, Canada T2N 1N4

Faculty of SCIENCE
Department of CHEMISTRY

Telephone (403) 220-5341

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Department of Energy Mines and Resources
CANMET Coal Research Laboratories
4500 - 16 Avenue N.W.
CALGARY, Alberta
T3B 0N6

Attention: Dr. R.N. Chakravorty
Scientific Authority

Dear Dr. Chakravorty:

Re: Detailed Study of the Reaction Mechanism of Spontaneous Combustion of Coal with Particular Emphasis on Western Canadian Low-Rank Coals.
DSS File. 01SG.23440-3-9162
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We take pleasure in submitting our final report on our study on the Mechanism of spontaneous combustion in Western Canadian low-rank coals. We would like to thank the Coal Research Laboratories of CANMET for sponsoring this study and for their advice and guidance throughout the term of this project.

Respectfully submitted,

F.W. Bachelor
Associate Professor
Department of Chemistry

FWB:lag
enclosure

Olympic Village and Speedskating - 1988

SUMMARY

This project was carried out under the auspices of Coal Research Laboratories of CANMET to study the reaction mechanism of spontaneous combustion of coal with special reference to Western Canadian coals. After an exhaustive review a number of critical parameters such as moisture, air, temperature, maceral and mineral content, peroxygen and free radical content were identified which appear to contribute to the causes of spontaneous combustion.

Eleven Western Canadian coals were selected for this study. These coals included one low volatile bituminous, six high volatile bituminous, three subbituminous and one lignite. All coals were submitted for petrographic, proximate, ultimate and trace metal analysis. With one exception, all high volatile bituminous and subbituminous coals examined have exinite contents of 5 percent or greater. All high volatile and subbituminous coal samples showed cobalt and manganese levels much higher than the low volatile bituminous or the lignite coals. Both of these metals are known to be active in the decomposition of peroxides. The low volatile bituminous coal had an equilibrium moisture content of only one percent while the high volatile bituminous coals had moisture contents of eight to twelve percent. Subbituminous coals were much wetter, running eighteen to twenty percent and the lignite contained almost thirty percent moisture. Oxygen content on dried coal samples followed a similar trend as moisture with the low volatile bituminous having an oxygen content of about five percent and the remainder ranging in order of decreasing rank to an oxygen content of twenty-four percent in the lignite. Sulfur levels were below one percent in all coals, however nitrogen reached levels between one and three percent in most of the high volatile bituminous

and subbituminous coals.

Treatment of crushed and sieved coal samples with an air or nitrogen flow of different relative humidities in an adiabatic apparatus gave data on the susceptibility of these coals to a temperature rise. With moist air or moist nitrogen, the temperature rise was found to be related to equilibrium moisture content of the coal, residual moisture content of the coal after partial drying, and the relative humidity of the flowing media. The highest responses were found when dried coals were treated with air of a relative humidity of 97%. The temperature rise increases with the increase in moisture and the maximum temperature rises were observed with those coals which had the highest equilibrium moisture. A comparison of the temperature rise of the high volatile bituminous and subbituminous coals showed that the temperature rise for these coals was not directly related to the residual moisture, but the residual moisture expressed as a percentage of the equilibrium moisture. Coals of different ranks with varying moisture content, including coals which were partially dried, showed little or no temperature rise when treated with dry air.

Tests on coal samples by Diffuse Reflectance Infrared Fourier Transform analysis produced only qualitative data. One sees a distinct decrease in the ratio of aromatic to aliphatic hydrogen atoms as the rank decreases from low volatile bituminous to lignite. The low volatile bituminous shows the lowest carbonyl content, characteristic of ketones and carboxylic acids, but, on the other hand, shows the highest phenolic or phenolic ether content for all of the coal samples. All other coals tested showed little variation in either of these latter two parameters.

The results seem to indicate that with dried coals and a moist air flow, there is a decrease in aliphatic protons, and an increase in phenolic or

phenolic ether groups. The carbonyl content during these experiments was extremely variable and no reliable conclusions were possible.

Titration of coal samples for peroxygen content indicated that high volatile bituminous coals averaged peroxygen concentrations significantly higher as compared to the low volatile coal samples. Further, subbituminous coals and lignite gave peroxygen values almost three times as high as the average high volatile bituminous coal. It is therefore evident that the peroxygen content of these coals increases with the decrease in coal rank.

In general, coal samples equilibrated at 97% relative humidity show little increase in peroxygen content when treated with air, wet or dry, however, coals with an equilibrium moisture content over 10% did show a slight increase. Partially dried coals, when treated with air with varying relative humidity showed an increase in peroxygen content, and the increase being greater, the drier the air.

Sequential gas flow experiments were carried out to find out whether the reactions between moisture and the coals was reversible.

High volatile bituminous or subbituminous coals were treated sequentially twice with moisture saturated nitrogen followed by moisture saturated air. The coal samples were redried between treatments. There is an indication that moisture does react irreversibly to a small extent in these reactions. It was also found that the peroxygen content of the samples were highest after the second oxygen free moist nitrogen treatment. This implies that there is another source of oxygen available to the coal for peroxygen formation and is probably that oxygen which is present in the coal.

A series of coal samples of different ranks (low volatile bituminous, high volatile bituminous, subbituminous and lignite) were examined for free radical content by Electron Paramagnetic Resonance. The spin concentration

varied by a factor of one hundred for these coals with the low volatile bituminous showing the highest. The high volatile bituminous sample had a spin concentration less than one twenty-fifth that of the low volatile bituminous coal and the subbituminous having about one fortieth. The lignite sample showed a significantly lower value than any of the other coals. In addition to the decrease in spin value from high rank to low rank, a corresponding shift in the g-factor is observed. The g-factor for the low volatile bituminous coal indicated that the free radicals are almost exclusively associated with carbon atoms, whereas a gradual shift to higher values with lower rank coals indicated that an increasingly higher percent of these free radicals were located on heteroatoms.

A comparison of spin values versus peroxygen content of the two subbituminous coals exmamined by sequential flow experiments showed that when the peroxygen concentration was highest, the spin concentration was lowest, and vice versa.

An examination of the spin data from the Electron Paramagnetic Resonance measurements also showed that there was not only a change in spin concentration, but also a change in the character of the radicals present. In some cases this change in character was reversible. Examination of the line shape of the spectra can show changes in exchange rates of the free radicals and in some cases this can be interpreted as a change from stable radicals to reactive radicals. Presently no explanation for the cause or nature of these radical changes is available, but this aspect forms the basis for future studies.

This study established a definite interrelationship between equilibrium moisture content, extent of drying and relative humidity of air. One of the most important factors seems to be percent reduction of the equilibrium

moisture. The formation of new peroxygen bonds and decrease in free radicals on treatment with either air or moisture suggest that a relationship beween these two may be a marker for studying the susceptibility of coal to spontaneous combustion, but data at the moment is insufficient to be conclusive. Because there is the possibility of getting further information on the nature of the free radicals formed in these studies, there is a good possibility that this information may be useful in understanding the mechanism of spontaneous combustion. Differences in maceral content and particular trace metals offer other possibilities for further studies, since there is a distribution of these parameters in the coals which make them appropriate areas of investigation.

In any further studies, the major emphasis should be placed on the interaction of moisture and air with the coals, and the role of peroxygen-free radicals toward the spontaneous combustion of coals. The research in these areas is likely to help in better understanding of the reaction mechanism of spontaneous combustion of coal.

RESUME

Ce project a été exécuté sous les auspices des Laboratoires de recherche sur le charbon du CANMET afin d'étudier le mécanisme de réaction de la combustion spontanée du charbon, en particulier les charbons de l'Ouest du Canada. Après un examen complet, un certain nombre, de paramètres critiques, tels que l'humidité, l'air, la température, la teneur en maceral et en minéral, et la teneur en peroxygène et en radicaux libres, ont été identifiés comme des facteurs qui semblent contribuer à la combustion spontanée.

Onze charbons de l'Ouest du Canada ont été choisis pour cette étude. Ces charbons comprenaient un bitumineux peu volatil, six bitumineux très volatils, trois sous-bitumineux et un lignite. Tous les charbons ont été soumis à des analyses pétrographiques, élémentaires, immédiates et à des analyses d'oligo-métaux. A une exception près, tous les charbons bitumineux très volatils et les sous-bitumineux étudiés contenaient 5% ou plus d'exinite. Tous les échantillons de charbon bitumineux très volatil et les sous-bitumineux avaient des concentrations de cobalt et de manganèse beaucoup plus élevées que le charbon bitumineux peu volatil ou le lignite. Ces deux métaux sont reconnus pour leur activité dans la décomposition des peroxydes. Le charbon bitumineux peu volatil avait à l'équilibre une teneur en humidité de seulement 1%, alors que les charbons bitumineux très volatils avaient une teneur en humidité de 8 à 12%. Les charbons sous-bitumineux étaient beaucoup plus humides, avec une teneur en humidité entre 18 et 20%, et le lignite en contenait presque 30%. La teneur en oxygène des échantillons de charbon séché suivait une tendance similaire à celle de l'humidité; ainsi le bitumineux peu volatil avait une teneur en oxygène d'environ 5%, et les autres se situaient, dans un order décroissant de classe, jusqu'à une teneur en oxygène

de 24% dans le lignite. La teneur en soufre était en dessous de 1% pour tous les charbons, alors que la teneur en azote atteignait des niveaux entre 1 et 3% dans la plupart des charbons bitumineux très volatils et sous-bitumineux.

Le traitement d'échantillons de charbons concassés et tamisés par circulation d'air ou d'azote contenant différents niveaux d'humidité, dans un calorimètre adiabatique, a fournie des données sur la sensibilité de ces charbons à une augmentation de température. Avec de l'air humide ou de l'azote humide, l'augmentation de température était reliée à la teneur en humidité à l'équilibre du charbon, à la teneur résiduelle en humidité du charbon après un séchage partiel, et à l'humidité relative du gaz en circulation. Les meilleures réactions ont été obtenues lorsque les charbons séchés ont été traités avec de l'air ayant une humidité relative de 97%. L'élévation de température s'accroissait avec l'augmentation d'humidité, et les élévations maximums de température ont été observées avec les charbons qui avaient la plus haute teneur en humidité à l'équilibre. Une compariaison entre l'élévation de température des charbons bitumineux très volatils et celle des sous-bitumineux a démontré que l'augmentation de température pour ces charbons n'était pas directement reliée à l'humidité résiduelle, mais à l'humidité résiduelle exprimée en pourcentage de l'humidité à l'équilibre. Les charbons de différentes classes avec différentes teneurs en humidité, y compris les charbons partiellement séchés, ont montré peu ou pas d'élévation de température lorsqu'ils étaient traités dans l'air sec.

Les tests sur les échantillons de charbon par analyse par transformation de Fourier de la réflectance diffuse en infrarouge, ont produit seulement des données qualitatives. On a observé une diminution distincte du rapport

d'atome d'hydrogène aromatique et aliphatique lorsque la classe décroit de bitumineux peu volatil à lignite. Le bitumineux peu volatil présente la plus basse teneur en carbonyl, caractéristique des cétones et des acides carboxyliques, mais, d'un autre coté, il présente la plus haute teneur en phénol ou éther phénolique de tous les échantillons de charbon. Tous les autres échantillons testés ont présenté peu de variation dans l'un ou l'autre de ces deux derniers paramétres.

Les résultats semblent indiquer que pour les charbons séchés et une circulation d'air humide, il y a une augmentation du nombre de groupes phénoliques ou éther phénolique. La teneur en carbonyle durant les expériences était extremement variable, et aucune conclusion valable n'a été possible.

Des titrages des échantillons de charbon pour la teneur en peroxygène ont indiqué que les charbons bitumineux très volatils ont en moyenne des concentrations de peroxygène plus élevées que les échantillons de charbon peu volatil. De plus, les charbons sous-bitumineux et le lignite ont donné des concentrations de peroxygène presque trois fois plus élevées que la valeur moyenne pour les charbons bitumineux très volatils. Il est donc évident que la teneur en peroxygène de ces charbons augmente avec une diminution de la classe de charbon.

En général, les échantillons de charbon équilibrés à une humidité relative de 97% ne montrent qu'une faible augmentation de la teneur en peroxygène lorsqu'ils sont traités dans l'air, humide ou sec. Par contre, les charbons avec une teneur en humidité à l'équilibre de plus de 10% ont montré une légère augmentation. Les charbons partiellement séchés, lorsqui'ils étaient traités dans l'air ayant une humidité relative variable ont montré une augmentation de la teneur en peroxygène, et cette augmentation est d'autant plus grande que l'air est plus sec.

Des expériences avec des circulations de gaz séquentielles ont été effectuées afin de découvrir si les réactions entre l'humidité et les charbons sont réversibles. Les charbons bitumineux très volatils ou sous-bitumineux ont été traités deux fois, d'abord avec de l'azote saturé en humidité, puis avec de l'air saturé en humidité. Les échantillons de charbon ont été resechés entre les traitements. Il y a une forte indication que l'humidité réagit irréversiblement jusqu'à un faible degré dans ces réactions. Aussi, la détermination de la teneur en peroxygène des échantillons était plus élevée après le second traitement dans l'azote humide, dépourvu d'oxygène. Ceci implique qu'il y a une autre source d'oxygène disponible pour le charbon pour former le peroxygène, et c'est probablement cet oxygène que est présent dans le charbon.

Une série d'échantillons de charbon de différentes classes (bitumineux peu volatil, bitumineux très volatil, sous-bitumineux et lignite) ont été étudiés pour leur teneur en radicaux libres par résonance électronique paramagnétique. La concentration de spin variait dans une proportion de cent pour un pour ces charbons, les bitumineux peu volatils montrant la plus élevée. Les échantillons de bitumineux très volatiles avaient moins d'un vingt-cinquieme de la concentration de spin du charbon bitumineux peu volatil, et les sous-bitumineux en avaient à peu un quarantieme. L'échantillon de lignite a montré une concentration nettement plus petite que tous les autres charbons. En plus de la diminution de la valeur de spin de la classe supérieure à la classe inférieure, on a observé un déplacement correspondant de la valeur "g". La valeur "g" pour le charbon bitumineux peu volatil indique que les radicaux libres sont presque exclusivement associés aux atomes de carbone, alors qu'un déplacement graduel vers des valeurs plus élevées pour les charbons de classe inférieure indique qu'un pourcentage

toujours plus élevé de ces radicaux libres est situé sur des hétéro-atomes.

Une comparaison des valeurs de spin et de la teneur en peroxygène des deux charbons sous-bitumineux étudiés dans l'expérience de circulation séquentielle a montré que, lorsque la concentration de peroxygène était la plus élevée, la concentration de spin était la plus basse, et vice versa.

Un examen des données de spin provenant des mesures de résonance électronique paramagnétique montre aussi que l'on n'a pas seulement un changement dans la concentration de spin, mais aussi un changement dans le caractère des radicaux présents. Dans certains cas, ce changement dans le caractère était réversible. Un examen de la forme de la courbe du spectre peut montrer des changements dans les taux d'échange de radicaux libres, et dans certains cas, ceci peut etre interprété comme un changement de radicaux stables en radicaux réactifs. A l'heure actuelle, aucune explication n'est disponible, quant à la cause ou la nature de ces changements de radicaux, mais cet aspect forme la base d'études futures.

Cette étude a établi une corrélation certaine entre la teneur en humidité à l'équilibre, le degré de séchange et l'humidité relative de l'air. Un des facteurs les plus importants semble être le pourcentage de réduction de l'humidité à l'équilibre. La formation d'une nouvelle liaison du peroxygène et la diminution des radicaux libres après traitement à l'air on à l'humidité suggère qu'une relation entre ces deux paramètres peut être un point de départ pour l'étude de la susceptibilité du charbon à la combustion spontanée, mais les données actuelles sont insuffisantes pour être concluantes. Puisqu'on a la possibilité d'obtenir des renseignements supplémentaires sur la nature des radicaux libres formés dans ces études, il existe une forte probabilité que ces renseignements puissent être utiles pour comprendre le

mécanisme de la combustion spontanée. Les différences dans la teneur en macéral et en certains oligo-métaux offrent d'autres possibilités pour des études futures, puisqu'il y a une distribution de ces paramètres dans les charbons, ce qui en fait un domaine d'étude approprié.

Dans toute étude future, l'emphase principale devra être mise sur l'interaction de l'humidité et de l'air avec les charbons et aussi sur le rôle de la teneur en peroxygène et en radicaux libres envers la combustion spontanée des charbons. La recherche en ces domaines pourrait contribuer à une meilleure compréhension du mécanisme de réaction de la combustion spontanée du charbon.

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INTRODUCTION

Historically, the irregularity in global attention paid to the potentialities of coal as a premium fuel has been due to the varying accessibility to petroleum (1). Interest in coal and coal research promptly fades whenever a major oil strike is made, such as the Texas oil discoveries in the 1920's and Middle East discoveries of the 1940's, however, every threat to the oil supply, such as occurred in 1973, spurs a renewal. Now we have an oil surplus, OPEC is in disarray, synthetic fuel projects are being scrapped and COAL is the king no more (2).

Yet knowledgeable groups associated with coal at different levels; e.g. federal (Energy Mines Resources; Energy Conservation Board); provincial (Alberta Research Council); academic (The St. Francis Xavier University of Antigonish, The University of Calgary, etc.) and significantly for the national economy, industrial (Mobil, Gulf, Exxon, etc.) agree that coal could stage a comeback, even sooner than anticipated. Accordingly, it is suggested that this may be the most opportune time to carry out research, on a non-crisis basis, to develop the necessary technology for efficient, hazard free use of coal in the future.

This obviously necessitates an in-depth study of coal to chemically characterize it and determine the cause of its reactivity in cases such as SPONTANEOUS COMBUSTION. This is prevalent in low-rank coals and the search for its causes and the subsequent fire hazards associated with its mining, transport and storage has been given a high priority.

Western Canadian coals, representing substantial deposits and conveniently accessible by strip mining (3), are mostly low-rank in nature and prone to spontaneous combustion. The occurrence of a number of incidences of

spontaneous combustion in the sub-bituminous or high volatile bituminous Western coals have been reported (4). Little information is available on the annual economic loss due to this phenomenon, however, these losses are probably of considerable magnitude and are reflected in the high insurance rates.

Western Canadian coals have relatively high clay and moisture content, however a major advantage lies in their low sulfur content (3). Almost all of them contain less than 0.5% sulfur and some are as low as 0.2%, as compared to the Eastern North American coals, some as high as 5.0%. At present, Western coals can be burned without special environmental control for the removal of sulfur and other deleterious elements. With the anticipated decrease in the availability of premium fuel and the expanding market of low-sulfur fuel, in our present environmentally conscious age, a renewed interest has triggered the potentials of processing more such low-ranked coals. However, the accompanying hazards of spontaneous combustion at ambient temperatures pose serious problems in its mining, storage and transportation.

Considerable global research has been conducted, in general, on the spontaneous combustion of coal, and some of the factors associated with this phenomenon have been identified, but the exact chemical reaction mechanism, which is essentially a coal-oxygen interaction, still remains obscure. A number of proposals for the reaction mechanism have been put forward based on the effects of these factors and the resultant products, but to date, no comprehensive explanation has been found.

The present review of the available literature pertaining to the Spontaneous Combustion of coal in general, as well as with special reference to low-rank coals has been prepared to illustrate the increased concern prevailing at the Federal, Provincial, and Industrial levels. Their goal is to

prevent such hazards and losses by concentrating their efforts on identifying the chemical reaction mechanism involved in Spontaneous Combustion, with the help of presently available modern analytical techniques.

LITERATURE REVIEW

The review is divided into the following sections:

I) Reaction mechanisms and products formed.

II) Factors participating in Spontaneous Combustion:

- a) Moisture
- b) Oxygen concentration
- c) Temperature
- d) Mineral composition
- e) Maceral composition

III) Applications and Interpretations of modern analytical techniques:

- a) Fourier Transform IR (FTIR) - Diffuse Reflectance FTIR (DRIFT)/ Photo-accoustic FTIR (PAIFT)
- b) Solid State NMR-Spectroscopy
- c) Electron Paramagnetic Resonance (EPR)
- d) X-ray Photoelectron Spectroscopy (XPS)

IV) Conclusion

V) Recommendation

I. Reaction mechanisms and products formed:

Spontaneous combustion of coal has drawn the attention of a number of research groups and over the last century, hundreds of papers have been published (5,6). Several possible causes of this heat generation have been considered; e.g. bacterial action (7), migration of gases and vapour (particularly the condensation of moisture), breakdown of pyrite, petrographic structure etc. All or any of these may have a contributory influence of varying importance. One attempt has been made to set up a model and a series of equations has been derived to parameterize temperature, porosity, moisture and several other parameters to describe the spontaneous combustion process

(8,9). It is, however, generally accepted that Spontaneous Combustion is due to an increased reaction between coal and oxygen.

This complex reaction mechanism between coal and oxygen appears to take place in a sequential manner with progressively increasing temperature (6,10-13). A sequence of peroxide formation, its decomposition and ultimate formation of stable oxygenated compounds has been proposed.

Peroxide formation drew the attention of research workers, as early as 1897, when Yohe (14), and Russell (15,16) detected the presence of peroxygen by observing the fogging of a sensitized photographic plate kept in contact with an oxidized coal in the absence of light. This was further confirmed by Yohe and Herman (17) and Yohe and Wilt (18), who observed a definite ability of an Illinois coal, exposed to air, to oxidize titanous chloride. Yohe also reported that this oxidizing power initially increased to a maximum and then decreased with the duration of exposure time to air, thus indicating the possibility of loosely held oxygen (perhaps peroxide type) as an intermediate in this oxidation process. Though the presence of peroxides could not be proved, the oxidizing reaction to Yohe and Wilson's solutions (19) indicated such to be the case. The presence of peroxygen was also independently observed by Jones and Townend (20) when oxidized coal reacted with ferrous thiocyanate. Over the past years the formation of peroxygen at low temperatures has been studied by several groups of research workers (6,11,21-27). Recently, a group of Russian workers have measured the catalytic effect of brown coals on the decomposition of dilute hydrogen peroxide solutions. A result of this study was a correlation between the limiting hydrogen peroxide concentrations and the tendency of the coal towards self-heating and combustion (28).

Chakravorty et al (11) found that the presence of water was essential for the formation of a significant amount of the complex containing the "active oxygen" and this could not be simply regarded as chemisorbed oxygen. Berkowitz (29) stated that the first stage of coal-oxygen reaction is the chemisorption of oxygen at readily accessible (aromatic and non-aromatic) sites on the coal surface. However, for the formation of peroxides this chemisorbed oxygen would need moisture either from the surroundings or produced from chemically combined hydrogen (20) in coal and these peroxides or hydroperoxides are capable of oxidizing ferrous thiocyanate (20), titanous chloride (18) and hydroquinone (30). Berkowitz (29) also reported that below 70°C rates of oxidation are generally low enough to be independent of coal rank and the coal-oxygen reaction does not proceed much beyond the formation of an acid functional group and the formation of peroxides decreases considerably when the hydrogen content of coal falls below 3% (31). Sevenster (32) also reported absorption of oxygen on coal to be a process of chemisorption, even at temperatures above -5°C and observed that even at 0°C a considerable portion of oxygen was bound irreversibly.

There has been general agreement among the research groups that the coal-oxygen reaction enters the second stage of the process when a distinct transition takes place at about 70°C (6,11,27,29). The course of the reaction has been reported to be due to the thermal instability of the peroxides formed. Chakravorty et al (11) reported decomposition of the peroxide complex above 70°C and the rate of decomposition increased with the rise in temperature. Chamberlain et al (6) also observed that 70°C is the critical temperature around which gases and vapours are produced, contributing to the gob-stink and further suggested that above 70°C spontaneous combustion is

inevitable provided sufficient oxygen is available. Berkowitz (29), while reporting on the thermal instability of peroxides above 70°C, suggested that at this stage, oxidation rates are now sufficiently high enough to be controlled by oxygen transport to the inner coal surfaces. The overall oxidation rates therefore become progressively more dependent on coal porosity and tend to fall with increasing rank or particle size. Peroxides form only transiently or not at all. This is in agreement with the findings of Chakravorty et al (11) who observed that the smaller the particle size the greater is the rate of formation and accumulation of peroxygen. Also, coals of higher rank with smaller inherent moisture and oxygen contents give lower concentrations of peroxygen. Chakravorty et al (11) also reported that at higher temperatures, e.g. at 80 °C, peroxygen concentration rises to a maximum according to the exposure time to atmospheric oxygen, and then decreases again.

The third stage of coal-oxygen reaction has been the generation of carboxylic acids as intermediates (6,11,24-26,29), which, with further increases in temperature, break down to carbon monoxide, carbon dioxide and water.

Based on the information collected, peroxide formation seems to be of prime importance. Different groups have postulated different reaction mechanisms for the formation and breakdown of the peroxides and the influence of the nature of the resultant products and temperature.

The coal-oxygen reaction mechanism resulting in peroxide formation definitely involves moisture available environmentally or generated out of chemically combined hydrogen in the coal (11,29). Temperature and oxygen partial pressure merely influence the rate of the oxidation reaction and the formation of resulting products. The chemical reaction mechanisms postulated

so far show either formation of unstable peroxides due to incorporation of molecular oxygen in the presence of moisture or abstraction of easily removable hydrogen. In both cases, it is via free radical formation, and this initial stage terminates with the formation of stable oxygen bearing end products.

In this vein Chamberlain (6) postulated the following basic mechanism involving hydrocarbon peroxide formation by a chain mechanism which finally decomposes into different oxidation products:

$$R\text{-}H + O_2 \longrightarrow R\bullet + HO_2^{\bullet}$$

$$R\bullet + O_2 \longrightarrow R\text{-}O\text{-}O\bullet$$

$$R\text{-}O\text{-}O\bullet + HO_2^{\bullet} \longrightarrow R\text{-}O\text{-}OH + O_2$$

$$R\text{-}O\text{-}O\bullet + RH \longrightarrow R\text{-}O\text{-}OH + R\bullet$$

The peroxide R-O-OH then can decompose in different ways depending on what 'R' represents e.g.

R = Tertiarly alkyl peroxides → Ketones and Alcohols

R = Secondary alkyl peroxides —low temp→ Ketone

—high temp→ Aldehydes & Alcohols

R = Primary alkyl peroxides ⟶ Formaldehyde + Aldehydes & Alcohols

R = Olefins (33) ⟶ Acids, Alcohols and Ketones

It can be observed that free radicals play an important role in initiating the chain reaction. Chamberlain et al (6) also reported that the concentration of all gases determined increased when benzoyl peroxide was used as a chain intiator to provide free radicals. This supported the reaction mechanism proposed for the initial oxidation of coal below 70°C.

Marinov (21-23) carried out extensive research to determine the reaction mechanism of the interaction of coal with oxygen at low temperatures. According to Marinov (22) self-ignition of coal is probably due to the burning of low-molecular weight products, initiated by aldehyde oxidation. It has been reported that coal, particularly in the presence of iron, can act as a catalyst for the air-oxidation of ethanol to acetaldehyde and acetic acid (34). However, Marinov (22) reported that some of the reactions involved in this process are endothermic in nature. He reports that Bogojavlenskii and Fel'dbrin (35) observed a fat coal self-heated in winter, which was found to be enveloped by ice within the coal pile in summer, the air temperature being above 20°C. Marinov (22) suggested that the endothermal development observed in his experiments were due to exclusive formation of H_2O_2. However, he also reported that this endothermicity is compensated for by the exothermic decomposition of H_2O_2, which together with the abstraction of hydrogen by free radicals, oxidation of aldehydes and low molecular weight product formation and hinderance of heat transfer in thick layers of coal could be the cause of self-ignition.

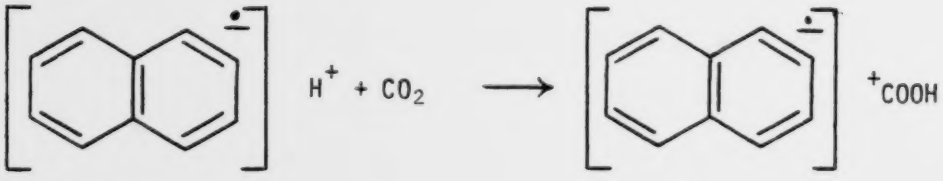
He postulated the following oxidative reaction pathways:

i) Oxidative reduction

Marinov explained this step, as has been done in the past, by several groups of research workers, as the formation of a peroxy complex and its decomposition to yield mainly carbon monoxide (36). According to Marinov, the region of predominant formation of carbon monoxide may be termed the region of "oxidative reduction".

Marinov (21), while explaining the mechanism of one-electron oxidation, postulated the appearance of a complex $[Ar\bar{\cdot}]H^+$ in coal which was subjected to

oxidation with molecular oxygen. He proposed that this complex could further react with carbon-dioxide like the metallation product $[Ar^{\bullet -}]Na^{+}$ of aromatic compounds:



I II

The complex I and II then interact or break down in different ways to yield carbon dioxide, carbon monoxide and water (22,38).

ii) Oxidative hydrolysis

Marinov (22) measured redox potentials of unoxidized and oxidized coal and surmised that oxidation causes an increase in its redox potential, but it acts as a donor of charge towards a system of water-oxygen.

Based on the above assumption, and that the aromatic part of coal can be considered as an acceptor of charge and hydrogen at a low degree of coal oxidation, the following scheme of oxidative hydrolysis, i.e. the interaction of the system water-oxygen with coal, has been proposed by him:

$$Ar + H_2O + RCHO \longrightarrow ArH_2 + RCOOH$$

or,

$$Ar + {}^{1}/_{2}O_2 + H_2O + 2RCHO \longrightarrow ArH_2 + 2RCOOH$$

$$2RCOOH + Ar \longrightarrow ArH_2 + 2CO_2 + 2R\bullet$$

$$2R\bullet + {}^{1}/_{2}O_2 + H_2O \longrightarrow 2ROH$$

$$ROH + Ar \longrightarrow ArH_2 + RCHO$$

where Ar is some aromatic system and ArH_2 its dihydro derivative.

iii) Oxidative dehydrogenation:

Marinov (22) further postulated that the acidic or basic sites of the oxidized coal catalyse the elimination of alcohols from ethers, in an endothermic reaction:

$$RCH_2CH_2OC_2H_5 \longrightarrow RCH{=}CH_2 + C_2H_5OH \qquad \Delta H = 50.6 \text{ kJ}$$

He also assumed the formation of hydrogen peroxide from hydroaromatic material like coal, and this reaction is also endothermic when the difference in resonance energy (ΔE_r) between the initial hydroaromatic and formed aromatic exceeds 8.4 kJ

$$ArH_2 + O_2 \longrightarrow Ar + H_2O_2 \qquad \Delta H = -8.4 \text{ kJ} + \Delta E_r$$

As stated earlier, Marinov attributed the cause for an ultimate exothermic process and self-ignition of coal to the number of exothermic reactions, e.g. decomposition of hydrogen peroxide, probably abstraction of hydrogen from the coal surface by free radicals and burning of low-molecular weight products initiated by aldehyde oxidation. He also stressed that the increasing layer thickness of coal plays a contributory role in this process by inhibiting heat-transfer. However the validity of the three mechanistic courses of oxidation postulated by Marinov are highly disputable and would need further justification.

In the mechanism of the proposed oxidative reduction, the author allowed himself to postulate the appearance of a complex $[Ar^{\bar{\cdot}}]H^+$ and proposes the scheme to be reminiscent of a mechanism proposed by Weissman et al (37), which in fact deals with metallation products. It is difficult to accept how molecular oxygen, which would strongly tend to accept an electron could donate an electron to the aromatic system. On the contrary, Weissman et al (37) dealt with the reaction which involved aromatic hydrocarbons and sodium

metal, a strong electron donating material. Marinov's (21) explanation of the formation of $[Ar\dot{-}]H^+$ is based on the increasing intensity of an infrared band at 800 cm^{-1} with a simultaneous decrease at 1600 cm^{-1} (aromat.). This evidence does not seem to be strong enough to justify the proposed electron donating capacity of molecular oxygen, which is contrary to the property of oxygen.

Further, Marinov's (22) postulation of alcohol elimination from the ethers of coal and the supporting mechanism seems to be controversial. Though Yokokawa's (23,38-40) experiments proved that part of the coal spin centres represent Bronsted acids, it is not convincingly explained that its protonation capacity would match the required levels of concentrated strong acids needed to produce the necessary conditions for the elimination reaction of alcohol from the relatively stable group of organic compounds such as ethers (41).

Marinov's mention of a fat coal enveloped by ice within the coal-pile (22), to support the endothermal development of coal oxidation seemed to contradict his own argument when he states that it is likely that the cause of endothermicity, which is the formation of H_2O_2, is compensated for by the exothermic decomposition of the same.

Bouwman and Freriks (24) studied coal-oxidation and monitored the reaction by infrared spectroscopy. They also concluded that the final products of the coal-oxidation are CO_2 and CO, however, there is an intermediary formation of arylcarboxylic acids, indicated by the increasing intensity of a band at 1700 cm^{-1}. They also reported on the basis of their infrared study (a weakening of the 1700 cm^{-1} band) that the formation of the carboxylic acid intermediates is probably the most exothermic oxidation step. They proposed

the following reaction mechanism for the coal-oxidation.

The release of the COOH group from the coal-matrix may then leave another reactive carbon site, where the cycle can start again. Carbon sites marked (*) are liable to oxidation. They emphasized the possible role water could play in the reaction, which induces the formation of hydroperoxide. They also reported, as have many authors before, the stages of oxygen chemisorption up to 70°C, then breakdown and formation of ultimate stable oxygenated compounds.

Liotta et al (25) interpreted the observations of peroxide formation at about 20°C by Jones and Townend (36) as an apparent initial generation of peroxy radicals, resulting from an interaction between the coal and molecular oxygen. This was supported by the compositional analysis, as it was found that the loss in hydrogen was at the rate of twice the pick up of oxygen, indicating hydrogen leaving as water. They found spectroscopic and chemical evidence of both aromatic and aliphatic ethers and proposed a reaction mechanism as follows:

Initiation: $-C-H \longrightarrow -C^{\bullet}$

$-C^{\bullet} + O_2 \longrightarrow -C-O-O^{\bullet}$

Propagation: $-C-O-O^{\bullet} + -C-H \longrightarrow -C-OOH + -C^{\bullet}$

hydroperoxide

$-C-H + \bullet OH \longrightarrow -C^{\bullet} + H_2O$

Radical

displacement: $-C-OOH + -C^{\bullet} \longrightarrow -C-O-C- + \bullet OH$

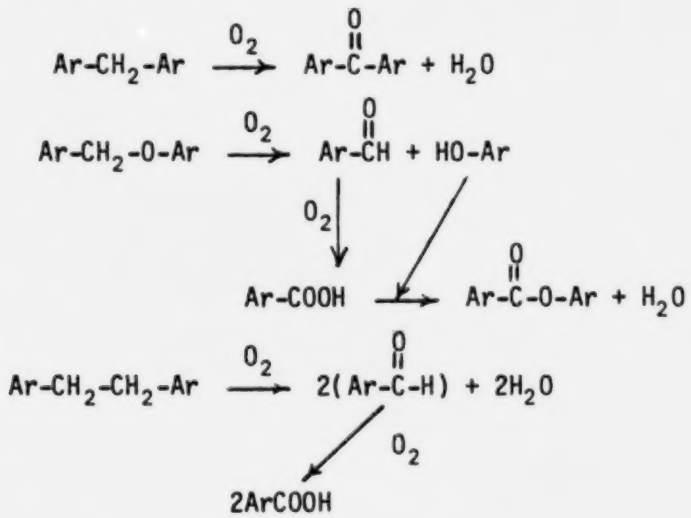
ether

Termination: $-C^{\bullet} + \bullet OH \longrightarrow -C-OH$

$2\ -C^{\bullet} \longrightarrow -C-C-$

Liotta et al (25) postulated that, to initiate the process a carbon radical is generated which is possibly oxygen or mineral matter assisted. The peroxy radical formed can abstract a hydrogen in the propagation stage. According to the authors, it is prerequisite for the radical displacement that the hydroperoxide radical and the carbon radical be in close proximity. Since they are formed simultaneously in the propagation stage, it is assumed they would be in close proximity.

Rhoads et al (26) carried out a low-temperature (60°C) oxidation study of coal, monitored it by a Fourier Transform IR-technique, and postulated the following reaction mechanism:



The mechanism of oxidation is interpreted in terms of classical autooxidation reactions and in which the initial formation of hydroperoxide, which either needs a light source or traces of radicals in the air, plays an important role (36,43). The hydroperoxide breaks down at the oxidation temperature. FTIR measurements showed loss in aliphatic CH, which indicated it to be the

initial site of abstraction of hydrogen and subsequent hydroperoxide formation. The schematic representation of the oxidation of other linkages (methylenic, ethereal) has been mentioned earlier.

Herring (7) referred to two important sets of reactions which seemed relevant to observations that low-rank coal has a greater tendency to ignite spontaneously than does coal of higher ranks. One of these reactions yields hydrogen rich volatile compounds, which normally have low activation energies for further oxidation and could release more heat on oxidation. The other reaction is the formation of highly reactive free radicals which are more easily produced in low-rank coals because of higher concentrations of H-, N- and O- compounds (sulfur should also be included as a highly potential generator of free radicals). The free radicals oxidize or facilitate oxidation of other compounds at temperatures not much higher than that of their own formation and consequently more heat is released. However, a mimimum temperature must be attained before the production of these commence, indicating that the coal would need some source other than free radicals to raise its temperature.

The importance of free radicals, their formation, and their involvement in the coal-oxidation process has been repeatedly mentioned during the course of this review. Recently (1984), Shendrik et al (43) reported that inhibitors of free radical reactions suppress the oxidation of coal at < 150°C.

II. Factors participating in spontaneous combustions:

a) Moisture:

From a review of the reports published by different research groups, it seems that there is no other single parameter known which contributes more

than 'moisture' to the cause of spontaneous ignition.

Qualitative support of its participation in this phenomenon of spontaneous combustion has been afforded by repeated observations that stockpiled coal often tends to heat up when exposed to rain after a period of dry, sunny weather (44,45), or when wet coal is placed on a dry pile (46,47), or where water is close as observed by strip-miners (e.g., in puddles in the floor of the pit or where melting snowbanks furnish a source of water)(7). The importance of this environmental or external contribution to the cause of spontaneous combustion has been significantly matched by the observations of several groups of research workers, who found that it is the low-rank coals with high 'inherent moisture' contents, which are most liable to spontaneous combustion (7,48-54).

The chemistry involved in this exothermic reaction mechanism and the important role of the moisture therein has been discussed in the previous section in detail, wherein its chemisorption on active sites on the surface of the coal, formation of peroxides and ultimate exothermic decomposition to CO_2, CO and H_2O via COOH functional groups was mentioned.

Moisture contributes to the spontaneous combustion of coal by another significant route, and that is the "heat of wetting". It has been discussed earlier that spontaneous combustion has been reported to be a complex reaction between coal and oxygen in a sequential manner with progressively increasing temperature (10-13). It is readily recognized that oxygen reacts combustibly with many organic molecules, among which coal is naturally included; yet this is not normally a spontaneous reaction and requires a certain amount of activation energy, usually in the form of applied heat.

The previous section dealt with the fact that the heat required to maintain the progressively increasing temperature could probably be generated by either individual or cumulative effects of all the chemical processes, e.g., decomposition of the peroxides, abstraction of hydrogen or free radical involvement. Yet even these processes would need further activation energies.

On correlating and interpreting the past and recent work, we tend to presume that this "heat of wetting" in conjunction with other chemical and physical parameters could be the triggering source of activation energy for this phenomenon of spontaneous ignition.

Berkowitz and Schein (53,55,56), in their experiments, have been able to demonstrate a significant increase in temperature from 25°C to 50°C, when moisture-saturated oxygen was passed through a 40g bed of dry lignite. They attributed this heat release, which could be equivalent to 85-105 J/g and cause a six to eight fold increase in oxidation rates, to the heat of wetting and not oxidation. Their inference was based on the fact that a virtually similar increase in the temperature was observed when moist, oxygen-free nitrogen replaced the moisture-saturated oxygen. Stott (57) carried out experiments to measure the heat of oxidation of coal in air of controlled humidity and also heat of desorption and sorption. He concluded that sub-bituminous coals always showed a greater loss of heat due to desorption of moisture than their rate of heat generation by oxidation. He also observed in another experiment that a sub-bituminous coal which was vacuum-dried to remove moisture (in a vacuum of 0.05 mm mercury at 105°C) and then subjected to a flow of moisture-saturated oxygen, fired spontaneously at an ambient temperature of 22°C within 30 min. Smirnova (58) has made similar observa-

tions where moisture considerably accelerates the oxidation process in high-volatile coals but has no appreciable effect on low-volatile coals. Hodges et al (50,51,59) carried out extensive research on the influence of moisture on the spontaneous heating of coal. Their review on past reports showed diverse postulations in the accelerating or retarding effect of humidity on the spontaneous combustion of coal.

Verselovskii (60) and Wolowczyk (61) separately concluded that the moisture absorbed from the air had an accelerating effect on the oxidation process. Jones and Townend (36) found that in the presence of moisture the reactivity of the chemisorbed oxygen with the formation of active hydroperoxide is quite high. Several workers (62-66) have also drawn conclusions that wetting of coal causes reduction in the rate of oxidation.

On the contrary, Winmill (67) and Hodges et al (50,68) found that with the sorption of water the temperature of coal may rise substantially. Berkowitz and Shein (53,55) suggested that the temperature of the coal in the vicinity of the actual sorption of moisture will be raised because of the latent heat of condensation consequently increasing the oxidation rate and heat generation and thereby providing an ideal situation for a potential fire to occur.

Hodges et al (50,51,59), in their work, carried out a series of experiments in an adiabatic calorimeter with different ranks of coals under variable conditions of inherent and environmental moisture, and concluded that depending upon the difference in the equilibrium humidities (inherent and environmental), the rate of temperature rise could show a five to ten fold increase or even more. Again it could as well show a drop in temperature, if the inherent moisture is more than the environment.

Guney (69) also carried out a series of experiments similar to Hodges (50,51,59) on the sorption and desorption of moisture on coal. He concluded as did Hodges (59), that the reaction mechanism involved in the spontaneous combustion of coal is via an unstable coal-oxygen or coal-oxygen-water complex which breaks down to CO and CO_2. Guney (69) further commented, there is reason to believe that the temperature increase due to self-oxidation is accelerated by wetting. Though the hydration of coal is an important factor, it is not a mandatory one, since, according to him, many coals would oxidize in the absence of water at a temperature slightly above ambient, however that would not be a cause of serious incidence. Bhattacharyya (70,71) also carried out experiments similar to Hodges (59) and Guney (69) on the role of sorption and desorption of moisture in the spontaneous combustion of coal. He too considered the different parameters, e.g., differences in the moisture equilibrium state, coal rank and particle size. His conclusion from a sorption experiment is that in a humid atmosphere, when simultaneous sorption of water vapour and oxygen takes place, the rate of heat generation in coal due to the sorption of water vapour is dependent on the equilibrium deficiency of the moisture of the coal (70). In his work on the desorption of moisture, he commented that as long as the partial pressure of moisture in the environment is lower than the coal surface, the chance of self-heating of the coal is less and the rate of heat loss due to the desorption of moisture is dependent on the equilibrium deficiency compared to the environmental moisture (71).

It is felt that the extensive work done by Bhattacharyya (70,71) and well supported by the finding of Hodges (59) and Guney (69), contribute significantly to the interpretation of the cause of spontaneous ignition, particularly with respect to the low-rank coals.

Battacharyya established from his experiments on coal samples of different ranks (B-high rank, D-medium rank, G and H-low rank), which are represented in curves shown in Figures 1-4, a relation between the parameters of coal rank and sorption (i.e. adsorption + absorption) as well as desorption.

Studies on coal constitution have shown that low-rank coals have a greater number of polar groups e.g. hydroxyl and carbonyl, which decrease with maturity and are almost absent in the anthracites (72). Further, evidence has also been put forward by other authors (73,74), suggesting that a part of water in coal is held by other than physical forces. Bhattacharyya (70) proposed that during the sorption process of moisture [which in fact is a combined effect of physical adsorption on the surface and bulk penetration of molecules into the structure of solids by diffusion (absorption)]., polar substances such as water immediately interact with the active groups in coal. This liberates more heat than that due to physical adsorption.

Bhattacharyya's (70,71) observations could be summed up into the following:

a) Moisture interacts with coal by the process of

i) physical adsorption; (heat of physical adsorptions: Q = 6 - 38 kJ/mole)

ii) absorption and chemical interaction with active polar groups which one could term as chemisorption; (heat of chemisorption: Q = 85 - 170 kJ/mole).

b) Porosity contributes considerably to the heat loss or heat release in different ranks of coal.

Sorption curves (70):

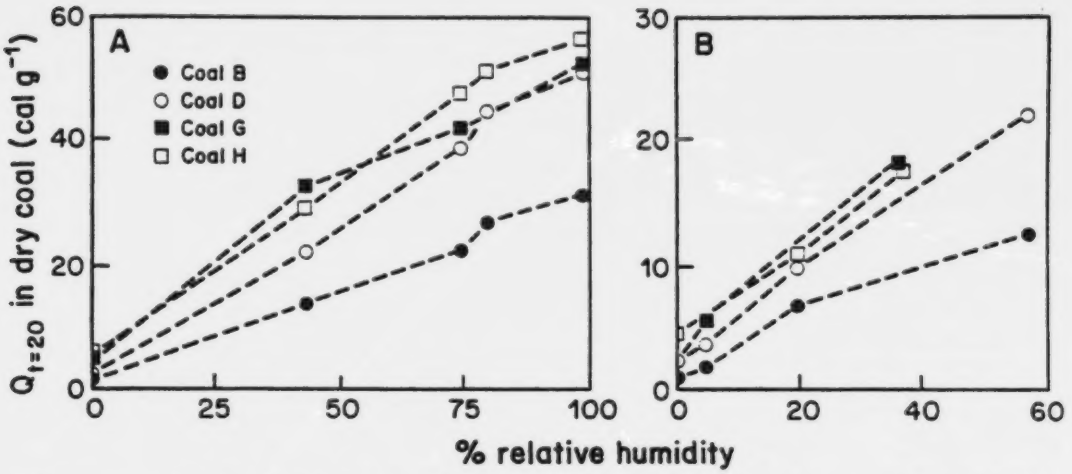


Figure 1. Variation in the characteristic heat release with the equilibrium moisture deficiency of the coals:

a) Test with dry coal
b) Test with moist coal

($Q_{t=20}$: Total heat produced in 20 hours of testing).

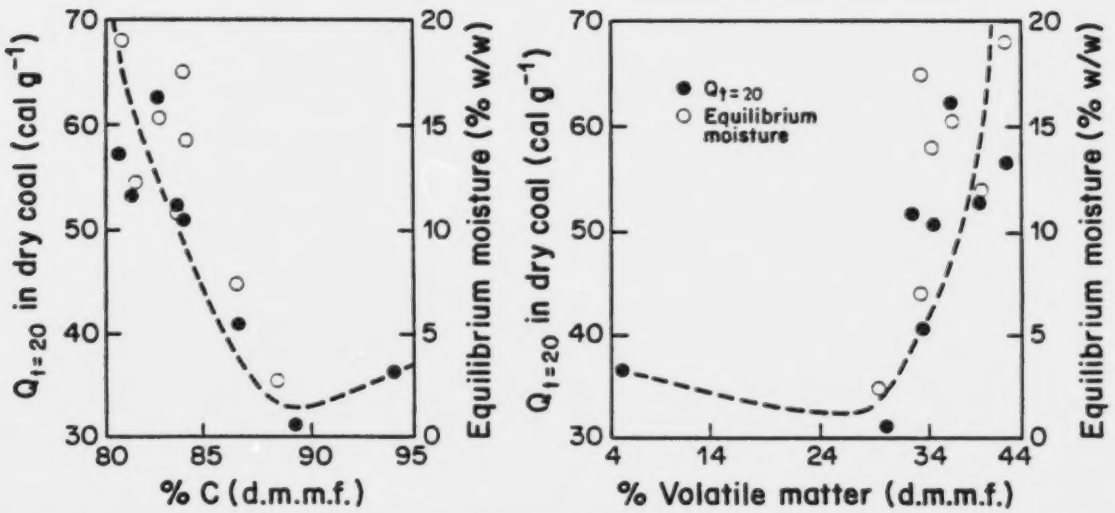


Figure 2. Variation in the characteristic rate of heat release and equilibrium moisture content with the rank of coal.

Desorption curves (71):

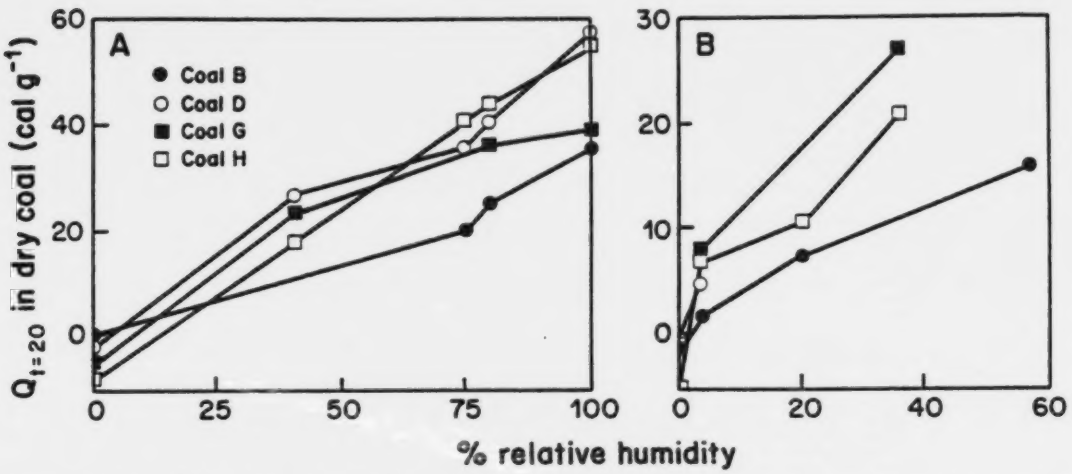


Figure 3: Effect of equilibrium moisture deficiency of air on the characteristic rate of heat loss from coals.

a) Test with dry air
b) Test with moist air

($Q_{t = 20}$: Total heat loss from a coal during 20 hours of an experiment).

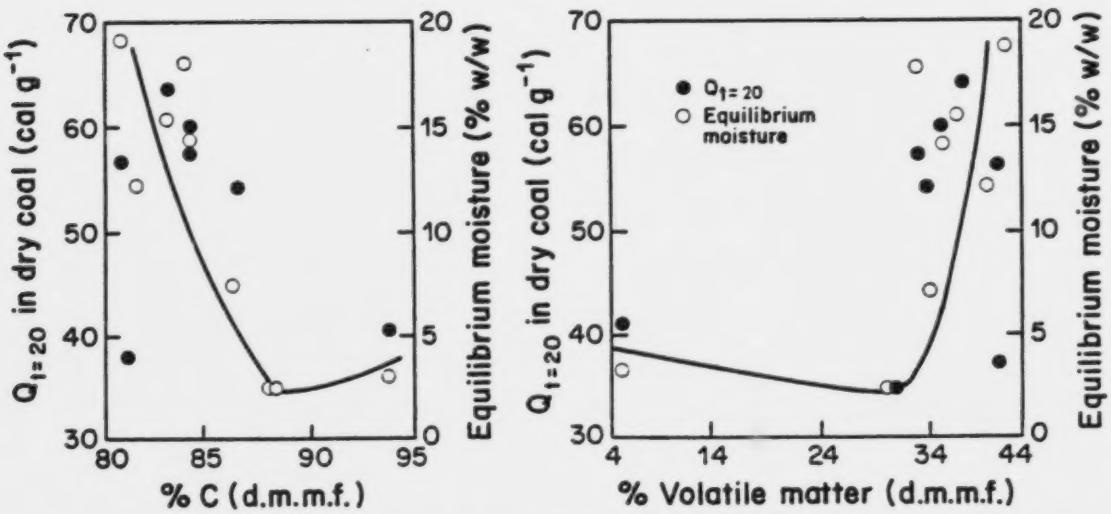


Figure 4: Variation in the characteristic rate of heat loss and equilibrium moisture content with coal rank.

Identification of Coals for Figures 1 and 3

Coal B: High-rank coal

Coal D: Medium-rank coal

Coal G: Low-rank coal

Coal H: Low-rank coal

Mention of active sites has also been made by Chamberlain (75) and Berkowitz (29).

Putting together all the above observations and considering the appreciable difference in the heat of physical adsorption and heat of chemisorption, one could probably find a reasonable cause for the greater liability of low-rank coals to spontaneous combustion than the high-rank ones.

It seems apparent that it is not the physical adsorption or the heat of wetting which determines the process of spontaneous combustion, rather it is the chemisorption which contributes most of the heat required to carry on the coal-oxygen reaction to the point of ignition. Heat of wetting could only be a supplementary contribution. This was further substantiated by the recent work of Nordon and Bainbridge (76), who observed that for normal moist coal (65% relative humidity), the heat of wetting could cause a temperature rise of only ~ 2°C, which according to them would be unlikely to contribute significantly to self heating of coal.

b) Oxygen concentration:

The role of oxygen in this coal-oxygen reaction has drawn the attention of research workers for a long time. Haldane and Meacham (77) reported that the rate of oxygen consumption at any moment was directly proportional to the residual partial pressure, when coal was kept at room temperature in a closed system. Van Krevelen (78) stated that the coal-oxygen reaction is of first order with respect to oxygen. Various other groups have also reported the effect of oxygen on coal-oxidation in the same line, however, they obtained varying exponential values for the rate of oxidation, under varying reaction conditions. Freshly mined coal immediately reacts with oxygen at a rate which is proportional to grain size and oxygen concentration. Moisture

was also shown to promote heating (79). Winmill (80-82) in his series of experiments, measured oxidation rates at constant oxygen pressure at a temperature of 30°C and observed that:

$$\text{rate of oxygen consumption is approximately } \alpha \text{ [oxygen concentration]}^{0.5}$$

Elder et al (83,84) found that in atmospheres containing 1-20% of oxygen and at 100°C (for a large number of coals):

$$\text{rate of oxygen adsorption } \alpha \text{ [oxygen concentration]}^{0.66}$$

Another study of low concentrations of oxygen on coal by Heemskerk (85) showed that long term storage of coals at oxygen concentrations of up to 20% resulted in loss of caloric value. He also showed that the addition of chemicals such as sulfuric acid or iron salts under these conditions stimulated the generation of heat. This study was also correlated with the moisture present and the gas flow rate.

Carpenter and Giddings (86) varied the partial pressure of oxygen in their experiments, however, maintained constant conditions of temperature, particle size and extent of oxidation. They found that varying oxygen content of the oxidizing medium influenced the rate of oxygen consumption in accordance with the equation:

$$\text{Rate } (R) = kp^n$$

$$\text{or, } \log R = n \log p + k' \text{ (constant)}$$

where the rate is expressed as the weight of oxygen consumed per unit weight of coal per unit time; p is partial pressure of oxygen in the oxidizing medium; n is the order of reaction with respect to oxygen and k is a constant. The fractional order of reaction obtained for 4 of 6 coal samples was 0.5. Rahman et al showed that the reaction was very dependent on particle size and for particles exceeding one millimeter in diameter, the rate is diffusion

controlled (87).

Chamberlain et al (75) stated that neither a small amount of air nor a high flow rate of air would cause ignition. Small amounts of air would keep the rate of oxidation of coal very slow, resulting in no appreciable increase in temperature, whereas a large flow of air through or over the coal would carry the heat away, restricting any increase in temperature and thus keeping the rate of oxidation at low levels. Thus experiments run by them under varying partial pressures of oxygen in the carrier gas (0.05 to 94.55%) showed that the absorption efficiency of coal towards oxygen increased as the partial pressure of oxygen in the carrier gas decreased, but the rate of absorption of oxygen by the coal at a given temperature was related to the partial pressure of oxygen in the carrier gas by the power law:

$$\text{rate oxygen absorbed} = d_1 [\text{oxygen}]^{n_1}$$

The values d_1 and n_1 were determined from the experimental data.

Sevenster (12) carried out adsorption experiments at low temperatures of -183°C to 80°C on coal samples, vacuum dried at 110°C for 6 hours. From the adsorption isobars obtained (Figure 5) he concluded that at a temperature of -80°C, physical adsorption predominates which diminishes with rising temperatures. This downward trend begins to flatten out at around -20°C to -10°C, the chemisorption of oxygen becomes appreciable at about -5°C and the chemical reaction sets in above 40°C. He further studied the heat of adsorption at temperatures of 0°C to 80°C in isothermal calorimeters. On the basis of the results obtained (Table I), he commented that the magnitude of the heat of adsorption indicated the adsorption process is of a chemical nature and chemisorption overshadows any physical adsorption even at 0°C. We feel this statement would have been more meaningful if the heat of adsorption had

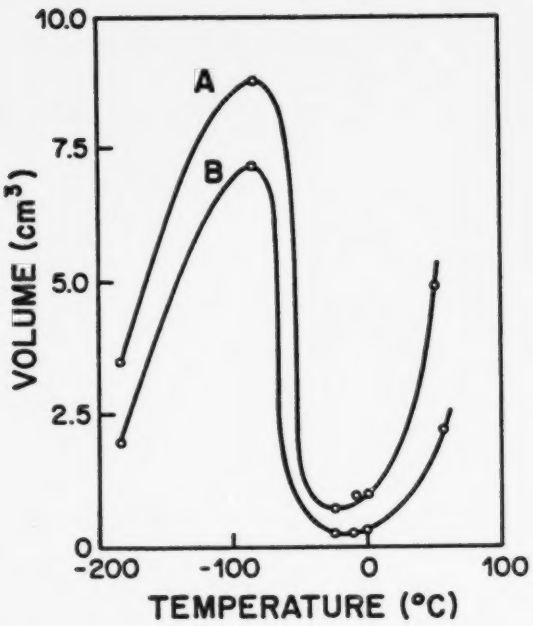


Figure 5: Adsorption isobars obtained at constant oxygen pressure (20 cm of mercury) (12).

Table I

Heat of oxygen adsorption by different coals and at different temperatures (average values of duplicate measurements) (12).

Time, (h)	Heat of adsorption, kcal/mole at								
	0°C			41°C			80°C		
	A	C	D	A	C	D	A	C	D
0.25	67	-	-	70	68	62	70	69	68
0.5	60	-	-	67	67	64	70	70	70
1.0	70	-	-	67	70	65	68	68	66
1.5	68	-	-	69	64	67	69	67	65
2.5	-	-	-	65	67	65	67	65	65
3.5	-	-	-	66	68	67	66	67	65
4.5	-	-	-	65	68	67	66	65	65

Table II

Activation energies in different temperature ranges and for different volumes of oxygen adsorbed (32).

Sample	Volume adsorbed cm^3	Activation energy, kcal/mole		
		30-50°C	50-70°C	70-90°C
A	0.05	4.5	2.2	8.0
	0.075	9.1	3.7	9.5
B	0.03	5.0	2.1	6.8
	0.04	8.3	1.9	-
C	0.05	5.0	2.3	3.3
	0.075	8.0	4.5	9.1
E	0.05	10.0	4.5	9.5

also been measured below -10°C. Sevenster (32) further reported that at the chemisorption stage, where it is the only significant process, the experimental results agreed with the Elovich equation (32). The integrated form of the equation is:

$$q = (2.3/\alpha) \log (t-t_o)/t_o \quad (1)$$

$$\alpha = 1/a\ t_o \quad (2)$$

where "q" denotes the amount of gas adsorped, "t" & "t_o" are time terms and "a" is the initial rate of adsorption as given by Equation 2. Equation (1) is applicable if one can obtain a straight line by plotting "q" against log $(t+t_o)$ with a suitable choice of t_o from trial plots. The applicability of the Elovich equation to the adsorption rates during the initial stages of adsorption on coal could also be determined from the dependence of the constants "a" and "α" on temperature and pressure.

It was observed that "a" generally tends to increase and "α" to decrease with rising temperatures up to 70°C, which is in accordance with the trends observed by Taylor and Thon (88). However, no conclusion could be drawn from the effect of pressure on these constants. He also commented that after the initial adsorption, chemisorption takes over, which then is the predominant rate-determining process. He observed that the activation energy always increases with the amount of oxygen absorbed (Table II).

Kaledin et al (89) observed that oxygen consumption below 57°C is of 1st order with an activation energy of < 20 kJ. Further they observed that below 57°C the combustion rate is dependent on the diffusion rate of oxygen.

Onitsuka and Watanabe (90) studied the spontaneous heating of 41 samples of coal and described the exothermic rate due to oxidation by the Arrhenius kinetic equation:

$$k = Ae^{(-E/RT)}$$

This rate increases rapidly at > 120°C. The frequency factor (A) increases as a 0.4-0.7 power of oxygen concentration in the atmosphere. In 1983 Takahashi et al (91) carried out studies on the low-temperature oxidation of various coal samples with a Differential Thermal Analyzer (DTA) under pressurized atmosphere and analyzed the results with a gas chromatograph. They observed that the rate of oxygen uptake is dependent on different factors, e.g., external surface area of coal particles, reactive maceral content (92) and temperature. Their emphasis on the influence of external surface area compared to total surface area including the internal one, indicates the importance of the role of surface area, which many previous authors have already reported (75,83,84,89). This also shows the need of extensive studies on the surface chemical reaction mechanism. The recent introduction of an advanced analytical technique involve X-ray Photoelectron-spectroscopy (XPS) to study the surface chemistry is gaining considerable importance and has now been applied on coal samples by several groups of research workers (93-96).

c) Temperature:

The previous section clearly indicates the strong independence of the rate of oxygen uptake or oxidation by coal on the temperature. Work of many of the authors has already been discussed in the previous section.

Olpinski and others (97) studied the effect of temperature on the irreversibility of the coal-oxygen reaction and established that the amount of oxygen recoverable decreases with the temperature at which adsorption takes place, becoming negligible at temperatures above 50°C. These findings were also confirmed by Sevenster (12,32).

Sevenster suggested that chemisorption of oxygen on the coal surface takes place in the temperature range of 20°C to 50°C and is fully the rate-determining factor in the very early stages of the adsorption process. In addition to the influence of oxygen concentration, the influence of temperature on coal oxidation was examined by several research groups. In general they agreed that an increase in temperature causes enormous increases in the rate of oxidation. Different research groups proposed different equations to justify their observations.

Scott (98) observed the oxidation rate increased enormously with increase in coal temperatures.

Schmidt (99) produced a series of parallel straight lines each corresponding to a particular temperature of oxidation. He derived a general relationship:

$$X = c\ t^{b}$$

where "X" is the amount of oxygen consumed in time "t", "b" is a constant dependent on particle size and "c" increases with temperature. Schmidt and Elder (83) found a factor of 1.7 for the rate of oxidation for each 10°C rise in temperature, whereas Chamberlain (75) found this factor to be 2 for each 10°C rise in temperature. Chamberlain (75) also reported that the important role playing active centres increase in number logarithmically with the rise in temperature, however this number is finite for a given surface area at constant temperature. The number of these active centres per unit area is less for high-rank coals than the low-rank ones.

The temperature around 70°C has been found by a number of research workers to be a critical one where the rate of coal oxidation takes a significant turn (6,12,26,29,32,75,88,89), and Chamberlain (6) already stated that

above this temperature, if sufficient oxygen is available, spontaneous combustion of coal appears inevitable.

d) Mineral composition:

Self-ignition of coals with high pyrite (FeS_2) content has already been reported. Mapstone (100) advanced a specific mechanism and postulated that oxidation of pyrite could produce pyrophoric ferrous sulfide as well as Fe^{++} and Fe^{+++}. Stored peat shows a high tendency toward self ignition as ion-exchanged iron concentration increases (101). These reactions would ultimately release about 840 kJ/mole and create regions near coal-to-pyrite interfaces at which coal oxidation could very easily become self-accelerating. Recent work of Sharma and Mirza (102) indicated that mineral matter present in coal could affect the reactivity of coal and could act as a promoter to different chemical reactions. Srinivasan and Seehra (103) observed from their Electron Paramagnetic Resonance (E.P.R) study on coals with and without pyrite and pyrrhotite that their presence causes an increase in the spin concentration, suggesting their participation in the formation of free radicals. However, this observation was made at a temperature > 150°C. It was also suggested by Cole et al (104) that mineral matter was responsible for the generation of free radicals in their pyrolytic and oxidative studies of 2 Illinois coals. Increases in free radicals were observed at all temperatures studied which were performed at 140° to 400°C. Weathered coal samples showed the largest increase in free radicals. We already discussed that free radicals could play a significant role in coal oxidation as has already been demonstrated by Chamberlain et al (6) in their experiments with benzoyl peroxide, a chain initiator providing free radicals.

Further, metal ions such as cobalt, iron and manganese have been reported to act as catalysts to increase the decomposition rate of hydroperoxides formed during the propagation step of a probable free-radical chain reaction in the coal oxidation process (105). Cobalt has even been reported to be a possible initiator of the free-radical formation. The general reaction mechanism of these metal ions in the above mentioned processes are as follows:

as catalyst in the hydroperoxide decomposition:

$$COOH + Co^{2+} \longrightarrow CO^{\cdot} + OH^{-} + Co^{3+}$$

$$COOH + Co^{3+} \longrightarrow COO^{\cdot} + H^{+} + Co^{2+}$$

as initiator or free-radicals:

$$C\text{-}H + Co^{3+} \longrightarrow C^{\cdot} + Co^{2+} + H^{+}$$

Recently Pong and Harris (106) demonstrated that impregnation of Victorian brown coal with cupric salts proved to be very effective in increasing the oxidation rate.

In a Russian study (107), it was found that the introduction of calcium ions into brown coal increased the low temperature oxidation rate. However, the suggestion that this is caused by the formation of calcium carboxylates which are unstable and decompose to ketenes at ambient temperatures seems rather unlikely. On the other hand another group of workers have reported that the addition of powdered calcium chloride causes a decrease in the oxidation rate of coal at temperatures ranging from 60 to 80°C (108).

e) Maceral composition:

Chamberlain et al (75,109) carried out an oxidation reaction rate study with the different macerals of different coal samples. The results, as shown in Table III, indicate the exinites have a much greater rate of oxidation, certainly above 75°C, than vitrinites or inertinites.

Similar observations were made by Takahashi (91), when he observed that a larger amount of total reactive macerals (e.g. vitrinite + exinite + 1/3 seminfusinite) was likely to be oxidized in a shorter period of time.

An investigation of Australian black coals also demonstrated that within a coal rank, an increase in the total vitrinite and exinite content increased the self heating propensity of the coal (92).

Herring (7) reported that Hanna No. 1 coal - a high volatile C bituminous to sub-bituminous A rank coal, which has a history of burning spontaneously, is unusual in that it has a very high exinite content (up to 16%). The reason or reasons, for the greater oxidation potential of exinites is not yet clear, however they do show gross similarities in their chemical structure, as described by Van Krevelen (110). A comparative study of the infrared spectrum of vitrinite and exinite fractions represented in Figure 6 indicates that exinite differs from vitrinite in that it contains more saturated C-H bonds, fewer aromatic C-C bonds and fewer aromatic C-H bonds. Exinites typically have higher H/C ratios in their structures than the other macerals, and these hydrogen-rich molecules are very likely more susceptible to oxidation.

III. Application of modern analytical techniques:

This review underlines the significant role chemical reactions play in the spontaneous combustion of coal. Therefore, a study on the chemical reaction mechanism becomes a subject of great importance to this process. This means that a detailed chemical characterization of coal is necessary. This has not been successful by degradation experiments, however improved experiments developed in recent years do show promise. The alternative approach of

Table III

Values of the reaction constant K x 10^{-3} (min^{-1}) for the oxidation of macerals (75)

Maceral	Morrison Brockwell (301)			Bernkely Botton Busty (602)			Bates Hutton (702)			Coventry bare (902)		
	50°C	100°C	150°C	50°C	100°C	150°C	50°C	100°C	150°C	50°C	100°C	150°C
Vitrinite	-	12	42	4	41	240	4	70	620	5	49	250
Exinite	-	86	620	4	110	1200	6	160	1450	23	200	310
Inertinite	-	2	21	3	35	150	4	48	380	3	120	-

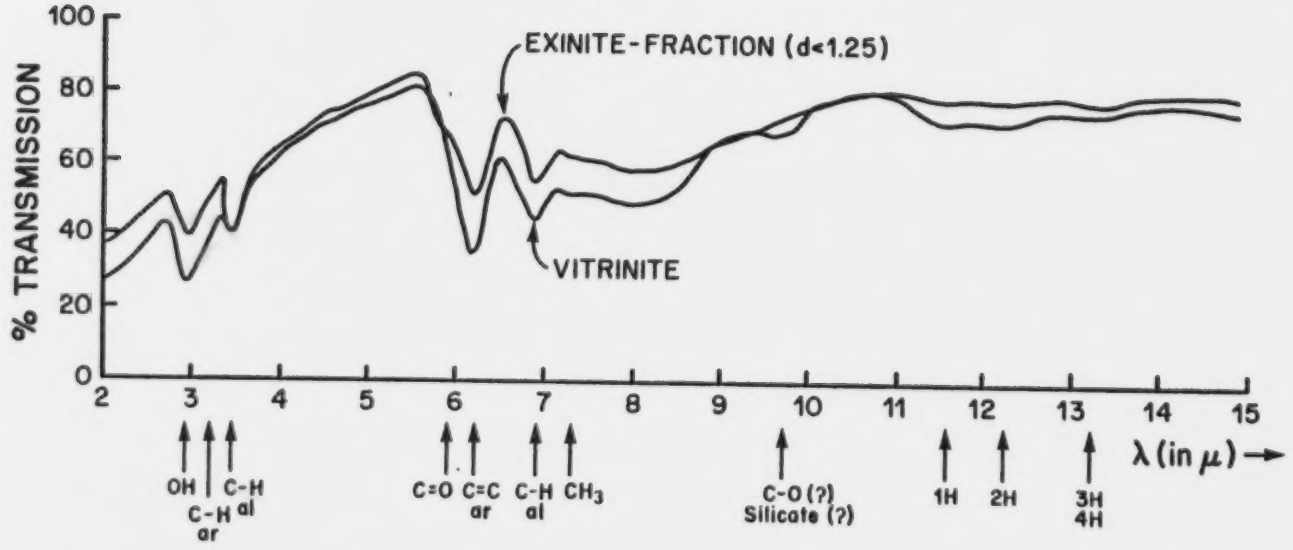


Figure 6: Infrared spectra of macerals from Yorkshire coal (110, p. 370).

direct characterization by analytical tools, e.g., IR, NMR, X-ray diffraction and scattering have been severely handicapped because of the opaque and non-crystalline nature of coal. Even the wet chemical approach has not been available to the chemists as coal is all but insoluble (1). However, recent advances in analytical techniques have provided the coal chemists the opportunity of overcoming the handicaps they have faced previously. A brief description of the scopes provided by the modern analytical techniques is presented here.

a) FTIR, PAIFT and DRIFT (111-130):

These techniques have been able to overcome substantially, the problems one experienced in IR dispersion spectroscopy by providing difference spectra before and after oxidation reactions, which permits one to evaluate the extent of changes taking place in the chemistry of the reacted coal samples. For example, FTIR has been used to follow the decomposition of carboxylic acid species to form a variety of new carbonyl species when two coal samples were preheated to 100°C and subsequently treated with oxygen (131,132). These methods can also eliminate the influence of moisture on the potassium bromide used to make the potassium bromide pellets of the coal samples (it is very difficult to make these moisture-free). Among the contributions of these advanced IR-Techniques is the assignments of the disputed 1600 cm^{-1} band to an aromatic stretching mode instead of the carbonyl group with the help of deconvolution of the coal spectra. Recently it has been suggested that one could calculate the aromaticity of coal samples by DRIFT analysis.

b) Solid state NMR Spectroscopy (133-135):

This technique has provided considerable information on the rank, maceral type, aromaticity and functional group analysis of coals. Obviously,

such information on coal samples, before and after oxidation reactions could contribute much to the coal oxidation reaction mechanism.

c) Electron Paramagnetic Resonance (EPR) (136-149):

EPR and its advances e.g. Electron Spin Echo Spectroscopy and Electron Nuclear Double Resonance Spectroscopy (ENDOR), are able to provide data which could lead to probable identification of still elusive free radicals already present in coal samples or formed during the oxidation reaction. In situ free radical studies could furnish valuable information on the coal-oxygen reaction (2), while it is in actual process. Free radical distribution in the maceral components of coal of different ranks could be determined and the relationship between the free radical concentrations and macerals derived. This information in turn would be helpful in identifying the role of free radicals in the coal oxidation reaction mechanism.

It has been reported that treatment of coals with calcium hydroxide causes a change in concentration of radicals and the g factor in their EPR spectra (150,151). The presence of a number of metal ions such as iron, manganese, copper and vanadium can also be followed quantitatively by EPR (152).

d) X-ray Photoelectron Spectroscopy (XPS) (93-96):

XPS also known as ESCA (Electron Spectroscopy for Chemical Analysis) instruments have been available since 1970, however, the technique has been used very little in the characterization of coal. Recently it has shown its potential role of complementing other spectroscopic techniques in determining the functional group composition. It has been applied to study the chemical nature of coal surfaces and also to study the coal oxidation reactions.

IV. Conclusion:

This review on the spontaneous combustion of coal presents the parameters which are likely to influence this generally recognized coal-oxygen reaction process, viz., moisture, oxygen, free radicals, temperature, maceral composition and mineral impurities. Further, the chemical reaction mechanisms suggested for coal-oxidation are found to be related by the progressive oxidative destruction of the non-aromatic part of the coal. This occurs over three stages: a) below 70°C, chemisorption of oxygen on readily accessible surface sites (aromatic and non-aromatic) with the formation of acidic functional groups, in particular, -COOH, phenolic -OH and rather unstable peroxides or hydroperoxides (in the presence of moisture), b) above 70°C, an increase in the rate of oxidation, breakdown of thermolabile and unstable peroxides and finally, c) rapid generation of humic acid, above ~150°C, and further breakdown and ultimate formation of CO, CO_2, H_2O and other low-molecular weight products at > 250°C.

Different partial pressures and different temperatures influence the coal-oxygen reaction mechanism, however, they only affect the rate of the process. The effect of differences in the moisture equilibrium between the coal and its environment seems to play an important role in the low-temperature oxidation of coal. A great deal of importance has also been attached to the participation of free radicals in this process, as well as to the availability of active sites or abstractable hydrogen atoms, depending upon the maceral composition of coal of varying ranks.

It is readily recognized that oxygen reacts combustibly with many organic molecules, which includes coal. However, this is not normally a spontaneous reaction and needs additional activation energy, usually in the

form of applied heat. This indicates that something abnormal and presently unrecognized, is happening to cause the spontaneous combustion of coal. Oxygen does not react spontaneously to form peroxides at ambient temperatures nor would it abstract hydrogen unless either the oxygen or the substrate has been previously activated. A review of the available literature shows that either this coal-oxygen reaction is responsible for peroxygen formation or it causes hydrogen abstraction, but it could not explain from where the needed activation energy for the peroxide formation comes. We feel that the key to this would be the universal explanation to the spontaneous combustion of coal, which so far has eluded the coal chemist, however significant contributions of important parameters e.g. moisture, oxygen, temperature, maceral distribution and minerals would have to be accounted for to explain the reaction mechanism of spontaneous combustion of coal.

The intent of this review was not only to compile the past work but to identify areas where further research is needed towards solution for unanswered questions regarding spontaneous combustion reaction mechanism of coals with particular emphasis on the Western Canadian low rank coals.

It was decided to plan and carry out studies with coal samples belonging to various ranks from Western Canada. The parameters chosen for this study were moisture, peroxy formation, free radicals, functional groups, maceral composition and mineral impurities. Accordingly experiments were planned whereby some of these parameters could be examined singly, concurrently and sequentially. The study will aim at explaining how these parameters influence the exothermic reaction which ultimately results in spontaneous combustion.

EXPERIMENTAL

I. Choice of coal samples:

Coal samples were collected to cover all ranks except anthracite as coal of this rank is not easily available and it is reported to be the least susceptible to spontaneous combustion. The samples included are low volatile bituminous (1 sample), high volatile bituminous (6 samples), subbituminous (3 samples) and one lignite. These were chosen as being representative of the major commercial coal types in Western Canada. Coal Research Laboratory, Calgary, CANMET, assisted in the collection of the coal samples.

II. Sample preparation:

Coal samples were crushed and sieved to a mesh size of -60 to +200. All operations were carried out under an atmosphere of argon to prevent oxidation. Later the samples were stored in glass bottles in an inert atmosphere.

Progressive drying of the coal samples A to D and K was carried out by equilibrating the samples at relative humidities of 97%, 58% and 20%, whereas samples E to J were initially equilibrated at a relative humidity of 97% and then progressively dried *in vacuo* over P_2O_5.

Residual moistures were determined by carrying out loss on drying on an aliquot of a representative sample at 105°C for 1 hour.

III. General coal properties:

Petrographic, Proximate, Ultimate and mineral constituents analysis were carried out on all the coal samples.

a) Petrographic analysis:

Petrographic analyses (Table IV) were done at the Institute for Sedimentary and Petroleum Geology, Calgary. It can be seen that the nine high volatile bituminous and subbituminous coals are quite similar with the exception of the low inertinite content for samples H and I. Coal A, a low volatile bituminous, shows a very low exinite content and an inertinite content which does not differ greatly from the high volatile bituminous and subbituminous coals; whereas Coal K, a lignite, shows both exinite and inertinite contents well below that of these coals.

b) Proximate analysis:

Proximate analysis (Table V) also shows little difference between these high volatile bituminous (B and E to I) and subbituminous coals (C, D and J) except for a wide variation in moisture content. The low volatile bituminous coal (A) is a fairly typical coal of this rank with low moisture (1%) and low volatile matter (27%) contents. On the other hand, the lignite has the highest moisture content (30%) and highest volatile matter (48%) contents. Ash contents were around 8 to 10% for all the coal samples except Coal A, which was found to be as high as 16%.

c) Ultimate analysis:

The degree of maturation of these coals can be seen from the oxygen content of the ultimate analysis (Table VI). Most of the high volatile bituminous and subbituminous show over 13% oxygen with the exception again of samples H and I. As expected the low volatile bituminous sample A is low in oxygen at 5.5% while lignite K contains 24% oxygen. It will be interesting to note that the hydrogen to carbon ratio did not vary significantly over the range of coals, and with a value no higher than 0.83, which indicates a high degree of aromaticity or of oxidation of the aliphatic side chains.

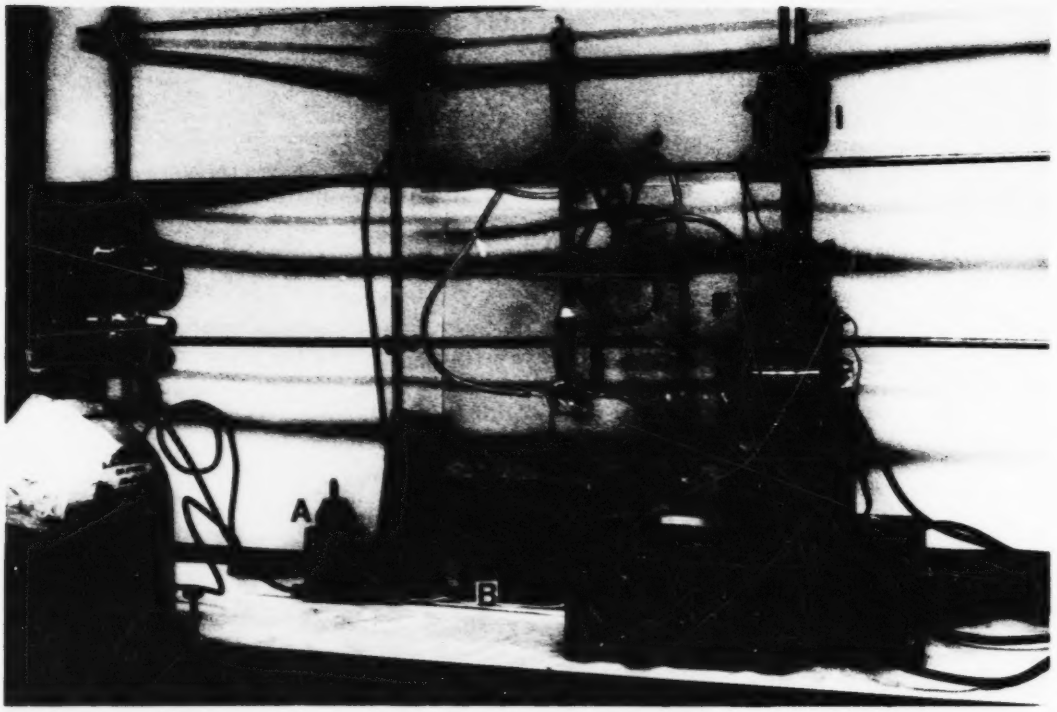
d) Mineral constituents:

Mineral analysis was carried out by Inductively Coupled Plasma Analysis (ICPA) and those which were considered to be of significance with regard to this study are reported in Table VII. These are cobalt, copper, iron and manganese. These elements are capable of interacting with free radicals or peroxides. Iron has frequently been suspect in the spontaneous combustion of coals, particularly in the form of pyrites (100). Both manganese and cobalt are known catalysts for peroxidic oxidations (105) and the addition of copper salts has been shown to increase the rate of spontaneous combustion in some Australian brown coals (106). Since the level of sulfur is low in all of these coals, the pyrite content must also be low. The amount of copper present in all the coals tested were found to be similar. Both manganese and cobalt are at significant levels in all high volatile bituminous and subbituminous coals examined and they are considerably higher than either the lignite or the low volatile bituminous coals.

IV. Adiabatic calorimetry tests:

25 g of the prepared sample were placed in the reaction vessel of the adiabatic calorimeter (Figure 7). The starting temperature was set on the heater and dry oxygen-free nitrogen was introduced at a rate of 20 ml per minute into the reaction vessel. When temperature equilibrium had been reached, the flowing media, i.e. oxygen-free nitrogen/air was allowed to pass through the coal. Two different rates of flow were used. During the first set, for coals A to D and K, a flow rate of 200 ml per minute was maintained. Further experiments indicated that a flow of 150 ml per minute resulted in greater rise in temperature. Accordingly for the second set, coals E to J, experiments were carried out using a flow rate of 150 ml per minute. The

Figure 7



(A) Flowmeter, (B) Flow-rate display

(C) Constant humidity vessel

(D) Relative humidity & Temperature probe;

(E) Relative humidity & Temperature display;

(F) Reaction vessel;

(G) Temperature display unit for the reaction vessel

(H) Dewar flask

(I) Mechanical stirring unit

(J) Rheostat

Not shown: Recorder and differential voltmeter

temperature of the bath was kept the same as the coal sample by a feedback mechanism activating heaters to raise the bath temperatures to that of the sample. In the cases where the temperature went below ambient, it was not possible to match this temperature, however, the changes were found to be insignificant. The flowing media were moisture saturated oxygen free nitrogen, moisture saturated air, and dry air. The temperature rise of the coal sample was monitored by a thermocouple placed in the middle of the coal sample and the temperature was recorded continuously over the full range of the experiment, usually 180 minutes.

"Sequential gas flow" experiments were carried out using the following procedure: Coal sample was placed in the reaction vessel of the adiabatic calorimeter. Moist nitrogen was passed through the coal for 180 minutes and the rise in temperature was recorded. Coal sample was taken out of the reaction vessel, dried over P_2O_5 *in vacuo*. This dried coal sample was again placed in the reaction vessel, moist nitrogen was again allowed to flow through it and the rise in temperature was recorded. The coal sample was taken out of the reaction vessel and dried *in vacuo* over P_2O_5. This dried coal was again placed in the reaction vessel. This time moist air replaced the moist nitrogen flow and rise in temperature was recorded.

In the "Moisture saturated air flow" experiments, the procedure was the same with only two runs using moist air.

Effects of changes in the relative humidities of the flowing media on the rise of temperatures over a period of 180 minutes were carried out on the five high volatile bituminous coals (E to I) and subbituminous coal (J). Air having relative humidities of 22%, 60%, and 97% was passed through progressively dried coal samples at the rate of 150 ml per minute for 180 minutes and rises in temperatures were recorded.

V. Functional group analysis:

The changes in the functional groups for the coal samples were examined by Diffuse Reflectance Infrared Fourier Transform spectroscopy using a Harrick Model DRA diffuse reflectance cell in a Nicolet 8000 FTIR spectrometer. Peak heights were compared in the absorbance mode and were compared to a standard background band of CO_2. DRIFT analyses were carried out on neat powdered coals placed, well packed, in the cell and subjected to 100 scans. In the past, coal samples have generally been prepared as KBr disks but some recent work have shown that infrared spectra of neat powdered coal can be measured directly by Diffuse Reflectance Spectrometry (115, 153). This technique not only cuts down considerably the amount of time required to prepare a KBr disc but also allows the possibility of measuring the spectra of reacting coals in situ.

VI. Peroxygen analysis:

The peroxide content in coal samples was determined by the titrimetric method of Chalishazar and Spooner (154). This method employs the oxidizability of peroxide groups present in coal with ferrous ammonium sulfate solution, to produce an equivalent amount of ferric ion. After the reaction between the oxidant in coal and the ferrous salt is complete (it is claimed that 15 minutes reaction time is sufficient), the ferric ion formed is titrated with a standard solution of mercurous nitrate adding excess ammonium thiocyanate. With every analysis of peroxy-complex in coal, a blank determination is carried out simultaneously using exactly the same procedure but without the coal sample to determine the ferric ion in the reagent and to annul the effect of errors of experimental technique.

VII. Free Radicals:

Free radical concentrations and g-factors were determined by Electron Paramagnetic Resonance (EPR) using a quartz tube (3 mm i.d. and 4 mm o.d.) in a 34 GHz (synchrodyne) spectrometer with 200 Hz magnetic field modulation and a TE_{101} cylindrical cavity or a 9 GHz (synchrodyne) spectrometer with 400 Hz magnetic field modulation and a TE_{011} cylindrical cavity.

RESULTS

I. Moisture saturated Nitrogen flow experiments:

The results of moist nitrogen flowing over the first set of coal samples, low volatile bituminous (Coal A), high volatile bituminous (Coal B), subbituminous (Coals C and D) and lignite (Coal K) are shown in Tables VIII to XII and in figure 8-11.

The high volatile bituminous and subbituminous samples (Coals B-D) showed very similar results but demonstrated a definite relationship between the temperature rise of the dried samples and the equilibrium moisture content of the coal samples. With progressive drying of the coal samples, the temperature rise increased significantly, increasing by almost 18°C in one case. Coal samples equilibrated at 58% relative humidity show insignificant increase over the moisture saturated samples, but when equilibrated at 20% relative humidity, a temperature rise of three to four times that at 58% relative humidity was observed.

The low volatile bituminous coal (Coal A) which had an equilibrium moisture content of 1.07% showed very little rise in temperature even on the dried sample.

A comparison of temperature rise of coal A to D after 180 minutes versus percent equilibrium moisture remaining in the coal samples is shown in Figure 12. Effects of progressive drying was quite significant. When subbituminous coals (C and D) were dried to less than 50% equilibrium moisture content, the increase in temperature was quite high. The curve also indicates that the rate of rise was quite significant. In comparison, high volatile bituminous coal (B) showed a higher initial rise followed by a slower rate of temperature increase.

II. Moisture saturated Air flow experiments:

A marked increase in both temperature rise as well as rate of rise is observed for all the coals (A to D and K) in their dried state, when the flowing media was changed from moist nitrogen to moist air. The results are shown in Tables VIII to XII and in Figures 13 to 17. Even samples equilibrated at 20% relative humidity showed small increases with the change in the flowing media. However, insignificant effects were observed for all the coal samples, when equilibrated at 58% and 97% relative humidities.

A comparison of temperature rise of coals A to D and K versus percent equilibrium moisture with the flowing media as moist air is shown in Figure 18. It followed the similar pattern as was observed in Figure 12, where the flowing media was moist nitrogen.

III. Dry Air flow experiments:

Dry air showed insignificant temperature effects on all the coal samples A to D and K. As can be seen in Table XIII the temperature effect is actually negative. Only the low volatile bituminous coal showed positive temperature changes over all moisture contents.

IV. Sequential experiments using Nitrogen and Air:

The objective of these experiments was to find out whether these treatments with air and nitrogen have physical adsorption, chemisorption or both effects on the coal samples. Sequential experiments were carried out on high volatile bituminous coal (B) and subbituminous coals (C and D) and the results are shown in Tables XIV to XVI. In all cases, the second treatment with moist nitrogen showed a decrease of 6-15% in temperature rise, as compared to the first treatment. The final treatment with moist air showed a

temperature rise almost as high as with the initial nitrogen treatment.

In another set of experiments the coal samples were treated with moist air, then dried, and later treated with either moist air or moist nitrogen (Tables XIV-XVI). In both cases a decrease in temperature rise ranging from 15 to 23% with moist nitrogen and 11 to 20% with moist air was observed. Since the temperature rise was less during the second treatment with moist air, this indicates that a partial irreversible coal-oxygen reaction is probably taking place.

V. Effect of Relative Humidity of flow media:

Results of air flow of varying humidities as well as dry air on five high volatile bituminous coals (E to I) and one subbituminous coal (J) are shown in tables XVII-XXII and Figures 19-42. In all cases temperature rise increased with increase in relative humidity of the flowing air and also with the decrease in percent residual moisture content in partially dried coals. With air flow at 22% relative humidity, in case of partially dried coals (70% of their equilibrium moisture) still showed a small negative response to air flow, whereas at 60% relative humidity, coal samples showed small positive responses even at saturated equilibrium moisture. With dry air on all coal samples at all residual moistures, coal temperatures decreased slightly.

VI. Effect of partial drying of coal:

Increase in temperature was also found to be closely related to the percent residual moisture in coal. It appears that such a rise does not depend on absolute residual moisture content, but on the percent of the equilibrium moisture remaining in the coal after drying. This is shown in figure 43. This graph shows the rise in temperature of the progressively

dried high volatile coal samples (E to I) and subbituminous coal sample (J) with 60% relative humidity air passing through them. It can be seen that a plot of temperature rise versus residual moisture (percent equilibrium moisture) is almost identical for all six of the coal samples tested. As evident from the results of the subbituminous coal J with an equilibrium moisture content of 19.5%, a temperature rise of 11.5°C was observed when its moisture content was reduced to ~30% of its equilibrium moisture content, whereas the same temperature rise of 11.5°C is reached by the high volatile bituminous coal E (equilibrium moisture content 8%) when it was dried to ~37% of its equilibrium moisture content only.

VII. Effect of varying Relative Humidity of flowing media on progressively drying coals:

A graph of the effect of relative humidity of the air flow versus residual moisture (% equilibrium moisture) on a high volatile bituminous coal sample (Coal I) is shown in Figure 44. In this figure one can notice the effect of relative humidity on partially dried coals. This coal sample when dried to 30% of its equilibrium moisture shows a temperature rise twice as great at 60% relative humidity as at 22%, and four times as great at 97% relative humidity.

This confirms that both moisture in coal and humidity of air play a major role in the spontaneous combustion reaction mechanism.

VIII. Functional Group Analysis:

The most useful method for identifying functional groups in organic molecules is infrared spectroscopy. This is normally accomplished by passing a beam of monochromatic light through a sample and measuring the amount of

light which is absorbed. Opaque samples such as coal present a problem which has been solved by the advent of intense laser light sources and a technique which involves reflectance of the incident light and measurement of the reflected light. In addition, the introduction of Fourier Transform Infrared spectrometers increases the sensitivity of the spectra by a rapid multiple scan technique which permits averaging of the background noise and thus gives a better signal to noise ratio. This allows considerable expansion of the usually weak spectra from coal samples and one can see the relevant functional group bands.

In spite of this, it is difficult to interpret many of the observed bands because coal is such a heterogenous material and the concentration of any one particular type of functional group is relatively small. Some groups, or types of bonds can be readily identified. This include carbon-hydrogen bonds as either aromatic or aliphatic hydrogens, hydroxyl functions, carbonyl groups (as acids, ketones or aldehydes) and other strong carbon-oxygen bonds.

The most useful purpose of these measurements in this work would be to examine the changes in the spectral windows for each functional group after the coal samples have had moist nitrogen or air flowing over them. The Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra of coal samples A-D and K are shown in Figure 45. All spectra are shown in the absorbance mode. A series of four spectral windows for these same coals are shown in Figures 46 to 49. These windows cover the ranges 3060-2860 cm^{-1} (carbon-hydrogen bonds, both aromatic and aliphatic), 1750-1550 cm^{-1} (carbonyl groups such as acids, ester and ketones, and carbon-carbon double bonds), 1510-1410 cm^{-1} (carbon-carbon bonds characteristic of aromatic rings), 1450-1150 cm^{-1} (carbon-oxygen bonds, particularly in esters and ethers). It should be rec-

ognized that other functional groups will also have absorption bands in these same regions.

As we progress from the low volatile bituminous coal A through high volatile bituminous coal B, subbituminous coals C and D and finally to lignite coal K there appears to be an increase in the ratio of aliphatic carbon-hydrogen bonds to aromatic carbon-hydrogen bonds. This is observed in the spectral window in Figure 46. When the band at 1204 cm^{-1} is examined, it appears to be more intense in coal A, whereas it is weaker and of relatively the same intensity for the other four coal samples. This suggests that phenols or phenolic ethers are of greater concentration in the coal A. Attempts to make correlations of any other bands were unsuccessful since no regular trends could be found when comparing these bands versus coal ranks.

The DRIFT spectra of coal sample B (a high volatile bituminous coal) during its exposure to the sequential moist nitrogen and moist air is shown in Figure 50, while the spectral windows for the same sequence are shown in Figures 51 to 55. Figure 55 is an additional spectral window at 1100 to 1000 cm^{-1} which is a characteristic region for hydroxyl groups.

Comparison of relative band intensities showed that changes were so small that it is not possible to say with any certainty whether changes are occurring in the concentration of the functional groups during these experiments. The only band which seems to be following a logical trend is that of the phenolic carbon-oxygen bond which shows no significant change when the coal sample was treated with moist nitrogen, but does show a small increase when subjected to a flow of moist air.

Coal sample B was dried and subjected sequentially to moist air flow, drying and a second moist air flow. The DRIFT spectra of these samples are shown in Figure 56 and the selected spectral windows in Figures 57 to 61.

Again, no significant conclusions can be drawn from comparisons of these spectral windows over the range of experiments except that possibly the phenolic carbon-oxygen bond may be increasing.

A similar set of experiments were run on subbituminous coal samples C and D and the DRIFT measurements made. As with coal B, no useful conclusions could be drawn from this data.

IX. Peroxygen Content in Coals

It is generally accepted that the reaction of oxygen with coals in presence of moisture initially produces peroxygen groups. Evidence for this has been observed and they have been quantitatively estimated by titration. In our titrimetric analysis of eleven coal samples we found a good correspondence between coal rank and peroxygen content. The low volatile bituminous coal (A) had a very low peroxygen content which was less than one tenth of the lowest content in any high volatile bituminous coal (B and E to I). This content increased through the subbituminous coals (C, D and J) to the lignite coal (K) which had a peroxygen content more than forty times as high as the low volatile bituminous coal (A). This data is shown in Table (XXIII). There is also a good correspondence between moisture content and peroxygen content. This can be seen in Figure 62 where a plot of peroxygen content versus moisture content shows an almost linear relationship.

The changes in peroxygen content were followed in the sequential moist nitrogen-moist air experiments. The high volatile bituminous coal (B) and the two subbituminous coals (C and D) all showed increases of peroxygen content when the dried coals were subjected to the first moist nitrogen flow. A second increase was observed when the redried coals were subjected to a second moist nitrogen flow. However, only the high volatile bituminous coal (B)

showed a further increase when subsequent moist air treatment was carried out. Both subbituminous coals (C and D) showed a decrease in peroxygen content at this stage. When the dried high volatile bituminous coal (B) was treated directly with a moist air flow it showed an increase in peroxygen content which was less than the overall increase form the sequential gas flow experiment described above. However, both of the subbituminous coal samples (C and D) showed little or no increase in peroxygen content when dried samples were subjected to a moist air flow. These results are shown in Table XXIV.

A series of experiments were carried out with moist air of different relative humidities being passed over moisture equilibrated coal samples (E to J). The relative humidity of the air flow was varied from 97% to dry air. Three high volatile bituminous coal samples (E, F and G), all with equilibrium moisture contents between 7.8 and 8.4% showed trends to decreasing in their peroxygen content as the relative humidity decreases, but all showed an increase or a return to near the initial value when dry air was passed over the sample.

On the other hand three coal samples, two high volatile bituminous (H and I) and one subbituminous coal samples (J), with equilibrum moisture contents of 11.6%, 12.4% and 19.5% respectively, showed increases of peroxygen content as the relative humidity of the air decreased at all levels of relative humidity. Subbituminous coal sample J showed the maximum increase of all of these samples with an increase of 16%. These results are shown in Table XXV.

These same coal samples (E to J) were dried and moist air of varying relative humidity ranging from 97% to dry passed over them. In all cases the trend was for the peroxygen content to increase although with high volatile

bituminous coal H (equilibrium moisture content 11.4%) a decrease was observed with air of relative humidity of 97%, and with high volatile bituminous coal I (equilibrium moisture content 12.4%) a decrease was observed with air of relative humidity of 97% and 60%. The overall rise in peroxygen content over that of the original dried coal samples varied from 9% to 38% and there is no obvious correlation between the coals and these values. These results are shown in Table XXVI.

X. Free Radicals in Coals:

It is known that coals contain not only peroxygen groups but also high concentrations of free radicals. The concentration of these radicals can be measured by Electron Paramagnetic Resonance (EPR) spectroscopy. This technique is capable not only of giving the concentration of the radicals, but also the nature of the atoms on which the free electrons are located and some information as to the environment of the atom. Because coal is such a heterogeneous system, it is more difficult to get highly specific information about the environment of the radicals, but it is possible to get some idea as to the types of atoms on which the free radicals are located.

The g-factor is an indicator of the location of the free radical from a value in these coals of 2.00227 for the low volatile bituminous coal (A), with a steady increase to 2.00299 for the lignite coal (K). It suggests that these radicals are located primarily on carbon atoms in the coal A to more and more on heteroatoms in the coal K (155). However, the actual concentration of these radicals is highest in the low volatile bituminous coal A and decreases to about one hundredth this concentration in the lignite coal K (See Table XXVII). Coal A also has the lowest heteroatom content, particularly with respect to oxygen. A graph of the g-factor as a function of

carbon and oxygen is seen in Figure 63. A graph of g-factor as a function of the total heteroatom is seen in Figure 64 (137). A typical EPR spectrum is shown in Figure 65.

When samples of high volatile bituminous coal B, and subbituminous coals C and D were dried and treated sequentially with moist nitrogen twice and finally with moist air in the "Sequential gas flow" experiments, it was found that the minimum radical concentration corresponded with the maximum peroxygen concentration (See Tables XXVIII to XXX and XXIV). This occured with the high volatile bituminous Coal B with the moist air treatment, but with both subbituminous samples C and D with the second moist nitrogen treatment.

One other interesting aspect of these radical measurements is the change in character of the radicals during the sequential gas flow experiments. Analyses of the EPR spectra in terms of lineshape and using Argand (DISPA) diagrams of d_o-a_o for various coals (Figures 66A-F; 67A-F; 68A-F) indicate significant changes in exchange rate of the radicals during the sequential flow experiments (156). The changes are not regular in these coal samples examined and in two cases, coals B and C, when treated directly with moist air, showed a very pronounced shift to a Gaussian curve. Surprisingly, all three coal samples, B, C and D, showed a return to a more typical Lorentzian lineshape after being treated successively with moist nitrogen twice and finally with moist air.

DISCUSSION AND CONCLUSIONS

The purpose of this project has been to carry out a detailed study of the reaction mechanism of spontaneous combustion of coal with particular emphasis on Western Canadian coals. In order to do this, it was necessary to examine a large number of parameters including the different ranks of coals in Western Canada. Many of the parameters which were measured were routine such as proximate analysis, ultimate analysis, trace metals and maceral composition. But some were not so routine. This latter group of parameters included peroxygen content, free radical contents, functional group analysis and most importantly, response to controlled flow of dry or moist air or nitrogen.

As can be seen from the review included in this report, a great deal of effort has been expended in attempting to determine the cause or causes of spontaneous combustion of coal, and each of the parameters mentioned here has been investigated to some extent, but usually only singly or in some cases a small number have been coinvestigated. This project has attempted to simultaneously coinvestigate all of these parameters so that a more complete picture of the total interactions may be seen.

Basically, the experiments in this project center around exposing different coal samples of varying rank from Western Canada to a series of flowing air or nitrogen streams of varying moisture, and measuring the changes which occur. These changes include temperature response, during the experiment, changes in peroxygen content and free radicals and changes in functional groups, particularly those containing oxygen. These changes are all directly related to the reactions between moisture and oxygen and the coal, and must be considered to be part of the primary causes of spontaneous combustion. The role that some of the other parameters such as trace metals

or maceral composition play can only be guessed at this stage and requires further investigation.

The moist air and moist nitrogen flow experiments pointed out several basic trends and interactions. The greatest temperature rises were observed when coals of high equilibrium moisture were dried and treated with moisture saturated air. Coals of lower equilibrium moisture contents when dried to the same moisture content did not show the same degree of temperature rise under the same conditions. This indicates that the extent of response is related more to the equilibrium moisture content of a coal sample than to the extent of drying. The examination of a number of high volatile bituminous and subbituminous coals of equilibrium moisture content between eight percent and thirty percent showed that similar response curves of temperature rise versus residual moisture (percent equilibrium moisture) were produced when subjected to a moist air flow. This indicates that a coal of high equilibrium moisture content which has been dried to 50% of its equilibrium moisture will show roughly the same temperature rise as a coal of much lower equilibrium moisture content which has also been reduced by half, in spite of the fact that the first coal will still have a very much higher residual moisture content.

In contrast to these results, when dry air or low moisture content air (22 percent relative humidity) was passed over coals of varying equilibrium moisture content, either saturated or dried, little temperature response was noted, which indicates that the moisture content in the flowing medium is also important, and the higher the moisture in the air, the higher the temperature response of the coal.

Air is not necessary to observe a temperature rise in these experiments. Flows of oxygen free moist nitrogen also caused an appreciable temp-

erature rise on dried coals, although the rise was not as great as with moisture saturated air. Some evidence was found that this oxygen free moisture can cause an irreversible reaction with coal. When a dried sample of coal was subjected to a moist nitrogen flow followed by drying and a second flow of moist nitrogen the temperature rise was less for the second moist nitrogen flow than the first. When this was followed by further drying and a flow of moist air, the temperature rise was only approximately equal to that of the first moist nitrogen flow, much less than if the coal sample had been treated with moist air in the first place. Since it is unlikely that moisture is reacting irreversibly at this temperature, it is probably acting as a transport medium for some other agent which does react. The most likely such agent would be the oxygen which is present in the coal.

Manifestations of the effects of the moist air and moist nitrogen flow experiments are expected to be found in the changes of peroxygen and free radical contents in the coals. One would also expect to find some changes in functional groups present in the coals since reaction with either moisture or oxygen should introduce new oxygen containing functional groups in the coal chemical structure.

Analyses of the coal samples showed that the peroxygen content increased with decreasing rank of the coals. The lowest peroxygen content was found in the low-volatile bituminous coal sample investigated while the highest peroxygen content was found in the lignite sample. The variation in peroxygen content between all of the high-volatile bituminous, subbituminous and lignite coals was not large but these all had peroxygen contents much higher than that of the low-volatile bituminous coal. In contrast, the free radical contents of the coals were found to be in the reverse order. The low-volatile bituminous coal had twenty-five times as high a concentration of free

radicals as a high-volatile bituminous coal sample and one hundred times as high a concentration as the lignite.

Although peroxygen content is probably a very good measure of the potential for spontaneous combustion of coal, free radical content is not. This is because the nature of the free radicals varies considerably and many of the radicals may be relatively unreactive, or of low reactivity in supporting oxidative combustion. This is typically characteristic of aromatic radicals which are the most prevalent in high rank coals. On the other hand the more reactive radicals tend to be associated with the heteroatoms which are more prevalent in the low rank coals. This is the pattern of free radicals found in the coals investigated. The low-volatile bituminous coal had a very high free radical content associated with carbon whereas the lower rank coals tended more toward free radicals localized on heteroatoms, as evident from their g-factors.

There appears to be some definite relationship between peroxygen and free radical content in coal. In the sequential treatment of coal samples B, C and D with moist nitrogen and moist air, it was found that when the peroxygen content increased, as it did in two cases with a moist nitrogen flow, the free radical content decreased, whereas when the peroxygen content decreased, as it did with moist air flow, the free radical content increased. This seems to imply that moisture alone catalyzes the conversion of free oxygen in the coal to peroxides, at the expense of the radicals originally present, whereas moist air is probably carrying the reaction beyond the peroxygen state.

E.P.R. (Argand) analysis showed a definite change in the nature of the free radicals. In the sequential flow experiments, an analysis of the line shapes of coal samples observed from E.P.R. studies suggest that the radicals are converted to a more reactive species but when treated successively with

moist nitrogen followed by moist air, the nature of the radicals returned to their initial state. When coals B and C were treated solely with moist air the radicals changed from stable to the reactive species but subsequently did not revert to the original state. This phenomenon requires further investigation.

Finally, it was hoped that any changes in the oxygen functional groups in the coal samples subjected to moist air or moist nitrogen could be observed by use of the powerful DRIFT analyses. In spite of the fact that high amplification of the spectra was used it was not possible to conclusively detect such changes. There were suggestions of some changes but the variability was too complex to draw any positive conclusions. This is not unreasonable since the reactions taking place in these experiments are relatively small on a molecular basis and because of the complexity of the coal sample, the changes would probably not stand out sufficiently to be able to separate any new spectral bands with any confidence. It is probable that this technique will only be useful when experiments are carried out where much greater changes result, as at higher temperatures.

The other parameters of possible significance, such as maceral, minerals etc. have not been tested with these experiments. However, the study showed all the samples with high temperature response to moist nitrogen and air contained relatively high levels of exinite with the exception of the lignite. The same can be said for the trace metal content of cobalt and manganese. These also were found to be relatively high in all of the high volatile bituminous and subbituminous coals, but low in the lignite and low volatile bituminous coals. These facts indicate the possible significance of these parameters in this reaction mechanism. We have projected that any or all of these parameters may be involved in spontaneous combustion of coal, but as yet, no direct correlations have been made.

RECOMMENDATIONS

This project has been an attempt to examine and identify those factors which contribute to the spontaneous combustion of coal, in particular, to the coals of Western Canada. This was done by studying the possible reaction mechanism from the standpoint of the variability of the coals examined and the parameters which could readily be used. As much as possible, the interactions between these parameters were correlated and gradually some suggestion as to a possible reaction mechanism began to emerge. However, the data is still too sparse and the sampling still too small to reach definitive conclusions. Virtually every result obtained was based on a single experiment and in many cases, the changes observed were so small that one has to interpret the results with caution.

In spite of this, some definite correlations between coal samples of different ranks, their moisture content, and their exposure to moisture and oxygen were observed. Further, there also appears to be some correlation between the peroxygen and free radical content in these coals, and the change when the coals are subjected to varying environmental conditions. What these changes mean is yet to be interpreted.

In order to carry this work further, the following recommendations are made:

1. A reasonable number of high volatile bituminous and subbituminous coals should be selected and a set of adiabatic calorimetry experiments carried out on these coals, varying both the moisture in the flowing media (air), and in the coals. These experiments should be carried out at least in triplicate so that some confidence in the results is assured.

2. The peroxygen and free radical content should be measured on the coal samples from recommendation 1 as soon as possible after the adiabatic

experiments are complete. This would minimize changes from long storage of the coal samples. Correlations between the free radicals and peroxygen should be made, and the nature of the free radicals examined by E.P.R. (Argand) analysis.

3. Coal samples subjected to moist air flow should be heated to 70°C to see the effect on free radicals, peroxygen content and possibly also functional group changes, as this is the temperature which many previous workers on spontaneous combustion state is the critical temperature. This experiment can also be carried out directly in the EPR spectrometer so that a monitoring of the free radicals is available over the entire temperature range.

4. Examine the effects of selected trace metals on temperature rise in the adiabatic experiments by either leaching them out of the coals or by increasing their concentration by soaking the coal samples in dilute solutions of the metals and then drying the samples. This type of experiment has been carried out on other trace metals by previous workers.

5. Attempt to isolate some reasonably pure macerals to examine the effect of moist air flow on their temperature rise. This should give some indication as to whether a particular maceral is more susceptible to spontaneous combustion than another. It might be necessary to add certain components back to the macerals, such as trace metals, to observe any complementary and appreciable effect.

6. Changes in porosity and permeability of the coals with drying should be monitored. These are parameters which have not yet been included in this study and this data would give a better understanding of spontaneous combustion phenomena.

The work recommended here could lead to the possibility of predicting the susceptibility of a particular coal to spontaneous combustion by measuring a selected number of parameters and correlating them with the results of this work. It should also lead to the ability to predict with some confidence the extent to which a particular coal could be dried safely for storage or shipping.

REFERENCES

1) Haggin, Joseph; Chem. and Eng. News, August 9, 1982, 17-26.

2) Petrakis, L.; Grandy, D.W. and Jones, G.L.; Chemtech, January, 1984, 52.

3) Patching, T.N.; Harrison, J.M.; MacKay, J.M. and Beck, R.A.D.; In "The Sleeping Giant - Coal Resources and Reserves", Canada West Foundation, Calgary, Alberta, November, 1980, 24-32.

4) Chakravorty, R.N.; Spontaneous Combustion Problems Associated with the Mining and Storage of Thermal Coals; Proceedings of the Second Technical Conference on Western Canadian Coals, June, 1982. (Published by the Canadian Institute of Mining and Metallurgy).

5) Chamberlain, E.A.C.; Hall, D.A. and Thirlaway, J.T.; Min. Engr., October, 1970, 121, 1-16.

6) Chamberlain, E.A.C.; Barrass, Gordon and Thirlaway, J.T.; Fuel, 55 (1970), 217-223.

7) Herring, J.R.; Proceedings of the 1983 International Conference on Coal Science, Pittsburgh, Pennsylvania, U.S.A., August, 1983, 754-5.

8) Schmal, D.; Duyzer, J.H.; Van Heuven, J.W.; Energy Res. Abstr. (1985) 10(10), Abstract No. 17860.

9) Schmal, Dick; Duyzer, Jan H.; Van Heuven, J.W.; Fuel, 64 (1985), 963-72.

10) Jones, R.E. and Townend, D.T.A.; Trans. Far. Soc.; 42 (1946), 297-305.

11) Chakravorty, S.L.; Long, R. and Ward, S.G.; Fuel, 29 (1950), 68-9.

12) Sevenster, P.G.; Fuel, 40 (1961), 7-17.

13) Olpinski, W.; Prace Glownega Inst., Gornictwa, Komun, 139 (1954), 3204.

14) Yohe, G.R.; Fuel, 29 (1950) 163-5.

15) Russell, W.J.; Proc. Roy. Soc.; 61 (1897), 424.

16) Russell, W.J.; Proc. Roy. Soc., 80, (1898), 376.

17) Yohe, G.R. and Harman, C.A.; J. Amer. Chem. Soc., 63 (1941), 555.

18) Yohe, G.R. and Wilt, M.H.; J. Amer. Chem. Soc., 64 (1942), 1809.

19) Yule, J.A.C. and Wilson, C.P.; Ind. Eng. Chem., Anal., 23 (1931), 1254.

20) Jones, R.E. and Townend, D.T.A.; Nature, London, 155 (1945), 424.

21) Marinov, Vassil N.; Fuel, 56 (1977) 153-7.

22) Marinov, Vassil N.; Fuel, 56 (1977) 158-164.

23) Marinov, Vassil N.; Fuel, 56 (1977) 165-170.

24) Bouwman, Robert and Freriks, Ivo L.C.; Fuel, 59 (1980), 315-322.

25) Liotta, Ronald; Brons, Glen and Isaascs, James, Fuel, 62 (1983), 781-791.

26) Rhoads, Carol A.; Senftle, Joseph T.; Coleman, Michael M.; Davis, Alan and Painter, Paul C.; Fuel, 62 (1983), 1387-1392.

27) Oreshko, V.F.; Isvest. Akad. Nauk SSSR. Otdel. Teck., Nauk; (1949), 748-759.

28) Spitsyna, N.G.; Niktin, K.N.; Kamneva, A.I.; Khim Tverd. Topl. (Moscow), (1984), (6), 50-53.

29) Berkowitz, N.; In "An Introduction to Coal Technology," Academic Press, New York (1979), 96-9.

30) Rafikov, S.R. and Sibiryakova, N. Ya.; Isv. Akad. Nauk. Kaz. SSSR Ser. Khim; 9 (1956), 13 [cf. C.A. 50 (1956), 8992].

31) Francis, W.; In "Coal," Arnold, London, (1961), 493-508.

32) Sevenster, P.G.; Fuel, 40 (1961), 18-32.

33) Muzyczuk, J.; Doctoral Thesis, Glowny Instytut, Gornictwa, Poland (1973).

34) Woog, A.; Compt. Rendu., 145 (1907), 124.

35) Bogojavlenskii, V.V. and Fel'dbrin, M.G.; In "Okislenie i Khranenie Tverdykh Goryuchikh Iskopaemykh," Transizdat, Moscow, (1958), 223.

36) Jones, R.A. and Townend, D.T.A.; J. Soc. Chem. Ind., 58 (1949), 197.

37) Paul, D.E.; Lipkin, D. and Weissman, S.J.; J. Amer. Chem. Soc., 78 (1956), 116.

38) Yokokawa, C.; 7th Int. Conf. on Coal Science, Prague (1968) Paper #2, 10.

39) Yokokawa, C.; Fuel, 47 (1968), 273.

40) Yokokawa, C.; Fuel, 48 (1969), 29.

41) Pine, S.H.; Hendrickson, J.B.; Cram, D.J. and Hammond, G.S.; In "Organic Chemistry," 4th Ed., (1980), 408-9.

42) ibid; pp. 886-7.

43) Shendrik, T.G. and Kompanets, V.A.; Khim. Tverd. Topl. (Moscow), (1984) (3), 45-8. [cf. C.A. 101 (1984), 75569].

44) Erdtmann, E. and Stoltzenberg, H.; Braunkohle, 7 (1908), 69.

45) Threlfall, R.; J. Soc. Chem. Ind., London, 28 (1909), 759.

46) Hoskin, A.J.; Purdue Univ. Experimental Station Bull., No. 30 (1928), 45.

47) Francis, W.; Fuel, 17 (1938), 363.

48) Rosin, P.; Fuel, 8 (1929), 66-78.

49) Yohe, G.R.; Illinois State Geol. Survey Rep., Invest. No. 207 (1958).

50) Hodges, D.J. and Hinsley, F.B.; the Mining Engineer, January, 1964, 211-224.

51) Robertson, W.M.; In "Disucssion," The Mining Engineer, January, 1964, 222.

52) ref. 29, p. 191.

53) Berkowitz, N. and Schein, H.G.; Fuel, 30 (1951), 94.

54) Smith, A.C. and Lazzara, C.P.; Chem. Phys. Processes Combust. (1984) 41/1-41/4.

55) Schein, H.G.; Brennstoff Chem., 32 (1951) 298-301.

56) Lowry, H.H.; In "Chemistry of Coal Utilization," 1st supplement, John Wiley and Sons, New York, (1963), 305.

57) Stott, J.B.; Nature, 188 (October 1, 1960), 54.

58) Smirnova, A.V. and Shubnikov, A.K.; Khim. i. Tekhnof. Topliva, i. Masel; No. 5 (1957), 40. [cf. C.A. 51 (1957) 18548].

59) Guney, M.; Hodges, D.J. and Hinsley, F.B.; The Mining Engineer, (November, 1969), 67-84.

60) Veselovskii, V.S.; Khim. i. Tekhol. Topliva. i. Masel; No. 5 (1957), 65 [cf. C.A. 51 (1957), 18547].

61) Wolowczyk, P.; Bergakademie, 12 (January, 1960), 4. (N.C.B. Transl. A 1915/A1).

62) Guney, M.; Coll. Guard., 216 (Jan.-Feb., 1968), 105-110.

63) ibid; p. 137-143.

64) Petrenko, A.P.; Report to 2nd All-Union Conf. on Storage of Solid Fuel; Abstract of reports, Moscow (1955).

65) Moore, B. and Sinnalt, F.S.; Fuel in Science and Practice, 4 (1925), 194-8.

66) Moore, B. and Sinnalt, F.S.; Fuel in Science and Practice, 5 (1926), 377-380.

67) Winmill, T.F.; Trans. Instn. Min. Engrs.; 48 (1914-15), 535-549.

68) Hodges, D.J. and Acherjee, B.; Trans. Instn. Min. Engrs.; 126 (1966-67), 121-131.

69) Guney, M.; The Canadian Mining and Metallurgical (CIM) Bulletin, (March, 1971), 138-146.

70) Bhattacharyya, K.K.; Fuel, 50 (1971), 367-380.

71) Bhattacharyya, K.K.; Fuel, 51, (1972), 214-220.

72) Lahiri, A. and Iyengar, M.S.; J. Sci. Ind. Res., India, 17A (No. 2) (1958), 60.

73) Mukherjee, P.N. and Lahiri, A.; Fuel, 36 (1957), 176.

74) Mukherjee, P.N.; Nandi, S.P. and Lahiri, A.; J. Sci. Ind. Res., India; 15B (No. 11) (1956), 638.

75) Chamberlain, E.A.C. and Hall, D.A.; Colliery Guardian, (February, 1973), 65-72.

76) Nordon, P. and Bainbridge, N.W.; Fuel, 62 (1983) 619-621.

77) Haldane, J.S. and Meachem, F.G.; Trans. Inst. Min. Eng.; 16, (1898-99), 457-492.

78) Van Krevelen, D.W.; In "Coal Science," Elsevier, Amsterdam (1957), 323.

79) Zetterlund, B.; Energy Res. Abstr., (1985), 10(b), Abstract No. 9540.

80) Winmill, T.F.; Trans. Inst. Min. Eng.; 46 (1913-14), 563-591.

81) Winmill, T.F.; Trans. Inst. Min. Eng.; 48 (1914-15), 503-507.

82) ibid., p.514-520.

83) Schmidt, L.D. and Elder, J.L.; Ind. Eng. Chem., 2 (No. 2) (February, 1940), 249-256.

84) Elder, J.L.; Schmidt, L.D.; Steinger, W.A. and Davis, J.D.; USBM TP, 681 (1945), 24.

85) Heemskerk, A.H.; Energy Res. Abst., (1985), 10(2), Abstract No. 1775.

86) Carpenter, D.L. and Giddings, D.G.; Fuel, 43 (1964), 247-266.

87) Rahman, M; Hasan, A.R. and Baria, D.N.; Proc. Intersoc. Energy Convers. Eng. Conf. (1985) 20th (Vol. 1), 1.631-1.642.

88) Taylor, H. and Thon, N.; J. Amer. Chem. Soc., 74 (1952), 4169.

89) Kaledin, N.V.; Al'perovich, V. Ya.; Pashkovskii, P.S.; Koshovskii, B.I. and Zaborskaya, A.N.; (USSR); Razrab. Mestorozhd. Polezn. Iskop. (Kiev), 92, (1982), 108-113. [cf. C.A. 99 (1983) 56140].

90) Onitsuka, Shigenori and Watanabe, Takanobu; Hitachi Zosen Giho, 43(1) (1982), 13-19. [cf. C.A. 97 (1982), 130320].

91) Takahashi, Katsumi; Uchida, Hiroyuki; Watanabe, Takashi and Takahashi, Kozumasa; Ishikawajima-Harima Heavy Ind. Co. Ltd., Tokyo, Japan 135. [cf. C.A. 100 (1984), 106206].

92) Moxon, N.T. and Richardson, S.B.; Coal Prep., 2(2) (1985), 91-105.

93) Grint, A. and Perry, D.L.; Proceedings of the 1983 International Conference on Coal Science, Pittsburgh, Pennsylvania, U.S.A., (August, 1983) 655-658.

94) Hirokawa, K. and Danzaki, Y.; Surf. Interface Anal., 6(4) (1984), 193-195. [cf. C.A. 101 (1984), 154543].

95) Perry, D.L.; Proceedings of NATO ASI, Antigonish, Nova Scotia, Canada, (August, 1984), in press.

96) Clark, David T. and Wilson, Rosemary; Proceeding of NATO ASI, Antigonish, Nova Scotia, Canada, (August, 1984), in press.

97) Olpinski, W.; cf. in Coward, H.F.; Saf.-i-Mines Res. Rep.; (1957) 142.

98) Scott, G.S.; USBM Bull., 455 (1944), 206.

99) Schmidt, L.D.; In "Chemistry of Coal Utilization," Ed. H.H. Lowry, John Wiley and Sons, Inc., New York (1945).

100) Mapstone, G.E.; Chem. Ind. (London), (1954), 658.

101) Lishtvan, I.I., Falyushin, P.L. and Kashinskaya, T. Ya.; Vestsi. Akad. Navuk BSSR, Ser. Khim. Navuk, (1985), (3) 94-6. [cf. C.A. 102 (1985), 116388].

102) Sharma, Durlubh K. and Mirza, Zulfikar B.; Fuel, 62 (1983), 916-7.

103) Srinivasan, Gopalan and Seehra, Mohindar S.; Fuel, 62 (1983), 792-4.

104) Cole, David A.; Herman, Richard G.; Simmons, Gary W. and Klier, Kamil; Fuel, 64 (1985) 303-6.

105) Wiseman, P.; In "An Introduction to Industrial Organic Chemistry," 2nd Ed., Applied Science Publishers, London, (1979), 97-111.

106) Pong, T.K. and Harris, I.J.; J. Inst. Energy, 57 (432) (1984), 383-7.

107) Neshin, Yu. I.; Sukhov, V.A.; Kraev, G.N. and Lukovnikov, A.F.; Khim. Tverd. Topl. (Moscow), (1984), (6), 54-8. [cf. C.A. 102 (1985) 48461].

108) Taraba, Boleslav and Harasta, Milovs; Acta. Mont., 67 (1984) 5-21. [cf. C.A. 103 (1985) 39524].

109) Chamberlain, E.A.C. and Hall, D.A.; The Mining Engineers (1972).

110) Van Krevelen, D.W.; In "Coal," Elsevier, New York (1961).

111) Rao, H.S.; Gupta, P.L.; Kaiser, F. and Lahiri, A.; Fuel, 41 (1962), 417-423.

112) Fujii, S.; Fuel, 42 (1963) 341-3.

113) Durie, R.A.; Shewchyk, V. and Friedel, R.A.; Fuel, 46 (1967), 53-8.

114) Painter, Paul C.; Snyder, Randy W.; Pearson, David E. and Kwong, John; Fuel, 59 (1980), 282-6.

115) Fuller, Michael P.; Hamadeh, Issam M.; Griffiths, Peter R. and Lowenhaupt, Douglas E.; Fuel, 61 (1982) 529-536.

116) Kuehn, Debbie W.; Snyder, Randy W.; Davis, Alan and Painter, Paul C.; Fuel, 61 (1982) 682-694.

117) Gethner, Jon S.; Fuel, 61 (1982), 1273-6.

118) Painter, Paul C.; Starsinic, Michael; Squires, Emily and Davis, Alan A.; Fuel, 62 (1983), 742-4.

119) Tooke, Philip B. and Grint, Alan; Fuel, 62 (1983) 1003-8.

120) Snyder, R.W.; Painter, P.C.; Havens, J.R. and Koenig, J.L.; Appl. Spectrosc., 37(6) (1983), 497-502.

121) Painter, P.C.; Davis, A.; Starsinic, M.; Koenig, J.L.; Havens, J.R.; Kuehn, D.W.; Snyder, R.W.; Senftle, J.T.; Rhoads, C. and Riesser, E.; Avail. NTIS from Energy Res. Abstr., 9(4), Abstract No. 5690.

122) Donini, J.C.; Proceedings of NATO ASI, Antigonish, Nova Scotia, Canada (August, 1984) in press.

123) Gaines, A.F.; ibid.

124) Lancaster, L.I.; ibid.

123) Lynch, Brian M.; ibid.

126) MacPhee, J.A.; Nandi, B.N.; Lynch, B.M. and Lancaster, Lai-Im; ibid.

127) Chien, P.L.; Markuszewski, R. and McClelland, J.F.; Preprints, Amer. Chem. Soc., Div. Fuel Chem., 30 (1985) 13-20.

128) Painter, Paul C.; Starsinic, Michael and Coleman, Michael; Fourier Transform Infrared Spectrosc., 4 (1985), 169-241.

129) Guiliano, M.; Mille, G.; Kister, J. and Dou, H.; Spectra 2000, 103 (1985) 35-9.

130) Fuller, E.L. Jr. and Smyrl, N.R.; Fuel, 64 (1985) 1143-50.

131) Gethner, Jon S.; Fuel, 64 (1985), 1443-6.

132) Gethner, J.S.; Appl. Spectrosc., 39 (1985), 765-77.

133) VanderHart, David L. and Retcofsky, H.L.; Fuel, 55 (1976), 202-4.

134) Havens, John R.; Koenig, Jack L.; Kuehn, Deborah; Rhoads, Carol; Davis, Alan and Painter, Paul C.; Fuel, 62 (1983) 936-941.

135) Axelson, David E.; Procceings of Nato ASI, Antigonish, Nova Scotia, Canada (August 1984), in press.

136) Petrakis, Leon and Grandy, D.W.; Anal. Chem., 50(2) (1978), 303-8.

137) Petrakis, Leon and Grandy, D.W.; In "Free Radicals in Coals and Synthetic Fuels," Elsevier, Amsterdam, 1983.

138) Das, Utpal; Doetschman, David C.; Jones, Paul M. and Lee, Myung; Fuel, 62 (1983), 285-8.

139) Khulbe, Kailash C.; Monoogian, Armen; Chan, Bei Wah; Mann, Ranveer S. and MacPhee, John A.; Fuel, 62 (1983), 973-4.

140) Dack, Stuart W.; Hobday, Malcolm D.; Smith, Thomas D. and Pilbrow, John R.; Fuel, 62 (1983), 1510-1512.

141) Dack, Stuart W.; Hobday, Malcolm D.; Smith, Thomas D. and Pilbrow, John R.; Fuel, 63 (1984), 39-42.

142) Silbernagel, B.G.; Gerhard, L.A.; Dyrkacz, Gary R. and Bloomquist, C.A.A.; ACS Symp. Ser. No. 252 (1984) 121-135.

143) Doetschman, David C.; Proceedings of NATO ASI, Antigonish, Nova Scotia, Canada, (August, 1984) in press.

144) Silvernagel, B.G. and Thomann, H.; ibid.

145) Khulbe, Kailash C.; Monoogian, Armen; Chan, Bei Wah; Mann, Ranveer S. and MacPhee, John Anthony; Indian J. Tech., 23 (1985) 263-5.

146) Cherepanova, E.S.; Lyubchenko, L.S.; Strigutskii, V.P. and Lukovnikov, A.F.; Khim. Tverd. Topl. (Moscow), (1985), (6), 15-19. [cf. C.A. 104 (1986), 36710].

147) Cherepanova, E.S.; Lyubchenko, L.S.; Navosha, Yu. Yu.; Strigutskii, V.P. and Lukovnikov, A.F.; Khim, Tverd. Topl. (Moscow), (1985), (6), 20-3.

148) Dack, Stuart W.; Hobday, Malcolm D.; Smith, Thomas D. and Pilbrow, John R.; Fuel, 64 (1985), 222-5.

149) Shida, Junichi; Itoh, Mamoru; Ogata, Takeaki and Kamada, Hitoshi; Bunseki Kagaku, 34(5) (1985), 243-7. [cf. C.A. 103 (1985), 39516].

150) Dack, Stuart W.; Hobday, Malcolm D.; Smith, Thomas D. and Pilbrow, John R.; Fuel, 64 (1985), 219-221.

151) Ogata, Tateaki; Mizuki, Kiyoshi; Saito, Tamaki; Shida, Junichi and Kamada, Hitoshi; Bunseki Kagaku, 34 (1985), 248-52. [cf. C.A. 103 (1985), 39517].

152) Evans, Jeffrey C.; Rowlands, Christopher C.; Barker-Read, Geoffrey; Cross, Robert M. and Rigby, Neal; Fuel, 64 (1985), 1172-4.

153) Wang, Shih-Hsein and Griffiths, Peter R.; Fuel, 64 (1985) 229-236.

154) Chalishazar, B.H. and Spooner, C.E.; Fuel, 36 (1957) 127-8.

155) Retcofsky, H.L., "Magnetic Resonance Studies of Coal" in "Coal Science, Vol. 1," edited by Gorbaty, M.L.; Larsen, John. W. and Wender, Irving, Academic Press, New York, (1982) 56.

156) Poole, Charles P. Jr., "Electron Spin Resonance", John Wiley and Sons, New York, (1983), 476, 492.

Appendix I - Description of Coal Samples

APPENDIX I

Description of Coal Samples

Sample #	Location	Rank
Coal-A	Alberta Mountains - Low volatile bituminous	lvB
Coal-B	Alberta Foothills - High volatile bituminous	hvb
Coal-C	Alberta Plains - subbituminous	sub
Coal-D	Alberta Plains - subbituminous	sub
Coal-E	Alberta Foothills High volatile bituminous	hvb
Coal-F	Alberta Foothills High volatile bituminous	hvb
Coal-G	Alberta Foothills High volatile bituminous	hvb
Coal-H	Alberta Foothills High volatile bituminous	hvb
Coal-I	Alberta Foothills High volatile bituminous	hvb
Coal-J	Alberta Plains - subbituminous	sub
Coal-K	Saskatchewan - Lignite	lig

Appendix II - Tables

Table IV

Petrographic Analysis of Coal Samples (on mmf. basis)

Coal	Reflectance %	Huminite%[a]	Exinite%[b]	Inertinite%
A	1.64	83.6	0.3	16.2
B	0.53	66.4	9.6	24.0
C	0.45	63.2	6.4	30.4
D	0.45	72.0	5.6	22.4
E	0.61	57.8	6.9	35.3
F	0.59	61.8	6.6	31.6
G	0.67	76.8	3.1	20.0
H	0.55	84.8	6.6	8.6
I	0.53	89.6	5.0	5.4
J	0.50	73.3	5.4	21.6
K	0.31	95.0	2.3	2.7

[a] low rank precursor of Vitrinite.
[b] synonymous to liptinite.

Table V

Proximate Analysis of Coal Samples

Coal	Equilibrium Moisture(%)	Volatile Matter(%) d[1]	Volatile Matter(%) daf.[2]	Fixed Carbon(%) d	Fixed Carbon(%) daf.	Ash(%)
A	1.07	22.61	27.18	60.57	72.82	16.82
B	7.83	34.87	39.23	54.02	60.77	11.11
C	18.23	32.55	36.32	57.08	63.68	10.37
D	20.55	34.23	36.69	59.06	63.31	6.71
E	8.02	39.01	43.90	49.86	56.10	11.13
F	8.36	37.23	41.56	52.36	58.44	10.41
G	8.21	36.87	41.42	52.15	58.58	10.98
H	11.65	40.29	44.25	50.76	55.75	8.95
I	12.51	39.70	44.54	49.43	55.46	10.87
J	19.49	39.09	43.65	50.47	56.35	10.44
K	29.97	44.50	48.10	48.02	51.90	7.48

[1] dry
[2] dry ash free

Table VI

Ultimate Analysis of Coal Samples

Coal	Carbon		Hydrogen		H/C	Nitrogen		Sulfur		Oxygen		Ash
	d[1]	daf.[2]	d	daf.		d	daf.	d	daf.	d	daf.	
A	73.42	88.27	4.20	5.05	0.69	0.49	0.59	0.52	0.62	4.55	5.47	16.82
B	68.75	77.34	4.03	4.53	0.70	0.49	0.55	0.25	0.28	15.37	17.30	11.11
C	67.72	75.56	3.56	3.97	0.63	0.19	0.21	0.12	0.13	18.04	20.13	10.37
D	69.30	74.28	3.79	4.06	0.66	0.42	0.45	0.22	0.24	19.56	20.97	6.71
E	70.73	79.59	4.86	5.47	0.83	1.13	1.27	0.15	0.17	12.00	13.50	11.13
F	70.38	78.55	4.44	4.96	0.76	1.00	1.12	0.09	0.10	13.68	15.27	10.41
G	66.85	75.10	4.34	4.88	0.78	1.06	1.19	0.20	0.22	16.57	18.61	10.98
H	75.35	82.76	4.96	5.45	0.79	1.96	2.15	0.21	0.23	8.57	9.41	8.95
I	70.84	79.48	4.90	5.50	0.83	2.40	2.69	0.38	0.43	10.61	11.90	10.87
J	65.78	73.45	4.38	4.89	0.80	2.55	2.85	0.29	0.32	16.56	18.49	10.44
K	65.23	70.50	4.01	4.33	0.74	0.30	0.33	0.77	0.83	22.21	24.01	7.48

[1] dry
[2] dry ash free

Table VII

Mineral Constituents in Coal Samples (ppm)

Coal	Cobalt	Manganese	Copper	Iron
A	<0.02	1.6	15.4	483
B	4.2	114.5	17.8	3433
C	5.5	37.1	8.4	679
D	5.7	76.7	5.0	2162
E	4.6	149.0	7.2	2643
F	6.6	89.8	9.3	2628
G	9.0	56.7	13.2	4046
H	4.9	35.4	6.1	2283
I	6.3	60.6	8.1	1705
J	6.4	35.1	13.9	1395
K	0.3	7.8	9.1	7408

Table VIII

Temperature rise (°C) with varying equilibrium moisture deficiencies with Low Volatile Bituminous coal A when treated with moist (~97% RH) gas flow.[1]
[Coal equilibrium moisture 1.07%]

Experimental Conditions	Moisture (%)	Time (min.)							
		0	30	60	90	120	150	180	Total Rise(°C)
		Temperature (°C)							
Moist N_2	1.07	24.0	25.1	25.7	26.3	26.9	27.5	27.9	3.9
Moist Air	1.07	24.0	25.2	25.8	26.3	26.7	27.2	27.7	3.7
Moist N_2	1.07	24.0	25.3	25.9	26.5	27.2	27.8	28.2	4.2
Moist Air	1.07	24.0	25.2	25.8	26.3	26.8	27.3	27.6	3.6
Moist N_2	0.59	24.0	25.2	25.8	26.5	27.2	27.9	28.3	4.3
Moist Air	0.59	24.0	27.5	28.9	29.8	30.7	31.3	31.6	7.6
Moist N_2	negl.	24.0	25.3	26.3	27.3	28.1	28.8	29.7	5.7
Moist Air	0.25	24.0	29.2	31.1	32.2	32.8	33.1	33.5	9.5

1) Moisture saturated flow of Nitrogen (oxygen free) or Air at the rate of 200 ml/min.

Table IX

Temperature rise (°C) with varying equilibrium moisture deficiencies with High Volatile Bituminous Coal B when treated with moist (~97% RH) gas flow.[1]
[Coal equilibrium moisture: 7.83%]

Experimental Conditions	Moisture (%)	Time (min.)							
		0	30	60	90	120	150	180	Total Rise(°C)
		Temperature (°C)							
Moist N_2	7.83	24.0	25.1	25.5	25.8	26.3	26.7	27.1	3.1
Moist Air	7.83	24.0	25.0	25.0	25.9	26.3	26.8	27.3	3.3
Moist N_2	7.08	24.0	25.2	25.7	26.4	26.8	27.4	27.9	3.9
Moist Air	7.08	24.0	24.6	25.2	25.8	26.5	27.0	27.4	3.4
Moist N_2	5.30	24.0	29.8	32.0	32.9	33.2	33.3	33.3	9.3
Moist Air	5.30	24.0	30.0	32.9	32.7	33.0	33.1	33.1	9.1
Moist N_2	3.93	24.0	33.4	36.4	38.1	38.8	39.0	39.0	15.0
Moist Air	2.91	24.0	35.4	40.1	42.4	43.3	43.6	43.7	19.7
Moist N_2	3.12	24.0	31.4	35.9	38.5	39.7	40.3	40.3	16.3

1) Moisture saturated flow of Nitrogen (oxygen free) or Air at the rate of 200 ml/min.

Table X

Temperature rise (°C) with varying equilibrium moisture deficiencies with Subbituminous Coal C when treated with moist (~97% RH) gas flow.[1]
[Coal equilibrium moisture: 18.23%]

Experimental Conditions	Moisture (%)	Time (min.)							
		0	30	60	90	120	150	180	Total Rise(°C)
		Temperature (°C)							
Moist N_2	18.23	24.0	24.7	24.8	24.9	25.1	25.1	25.1	1.1
Moist Air	18.23	24.0	25.1	25.2	25.2	25.1	25.0	25.0	1.0
Moist N_2	11.72	24.0	25.4	26.1	26.3	26.4	26.5	26.6	2.6
Moist Air	11.72	24.0	24.4	25.8	26.1	26.3	26.4	26.4	2.4
Moist N_2	7.09	24.0	29.9	32.8	34.2	34.7	35.0	35.0	11.0
Moist Air	7.09	24.0	31.0	34.0	35.3	35.8	35.9	35.9	11.9
Moist N_2	6.25	24.0	34.4	38.8	40.6	41.4	41.8	41.9	17.9
Moist Air	4.61	24.0	35.5	42.1	45.3	47.0	47.6	47.8	23.8
Moist N_2	4.62	24.0	32.6	38.1	41.8	43.6	44.2	44.8	20.8

1) Moisture saturated flow of Nitrogen (oxygen free) or Air at the rate of 200 ml/min.

Table XI

Temperature rise (°C) with varying equilibrium moisture deficiencies with Subbituminous Coal D when treated with moist (~97% RH) gas flow.[1]
[Coal equilibrium moisture: 20.55%]

Experimental Conditions	Moisture (%)	Time (min.)							
		0	30	60	90	120	150	180	Total Rise(°C)
		Temperature (°C)							
Moist N_2	20.55	24.0	24.8	24.9	24.9	24.9	24.9	24.9	0.9
Moist Air	20.55	24.0	24.6	24.8	24.9	25.0	25.1	25.2	1.2
Moist N_2	14.95	24.0	25.0	25.6	25.9	26.1	26.2	26.3	2.3
Moist Air	14.95	24.0	26.0	26.5	26.9	27.0	27.2	27.2	3.2
Moist N_2	9.92	24.0	33.3	33.5	34.5	34.8	34.8	34.8	10.8
Moist Air	9.92	24.0	31.3	34.2	35.5	36.2	36.7	37.0	13.0
Moist N_2	6.98	24.0	33.0	37.6	40.0	41.0	41.2	41.2	17.2
Moist Air	5.79	24.0	32.7	38.1	40.9	42.5	43.4	43.9	19.9
Moist N_2	5.00	24.0	31.2	36.4	39.9	41.9	43.0	43.4	19.4
Moist Air	4.99	24.0	35.9	41.9	45.1	46.9	47.8	48.0	24.0

1) Moisture saturated flow of Nitroge (oxygen free) or Air at the rate of 200 ml/min.

Table XII

Temperature rise (°C) with varying equilibrium moisture deficiencies with Lignite Coal K when treated with moist (~97% RH) gas flow.[1]
[Coal equilibrium moisture: 29.97%]

Experimental Conditions	Moisture (%)	Time (min.)							
		0	30	60	90	120	150	180	Total Rise(°C)
		Temperature (°C)							
Moist N_2	29.97	24.0	25.3	25.5	25.8	25.9	26.1	26.3	2.3
Moist Air	29.97	24.0	25.0	25.3	25.6	25.8	26.0	26.2	2.2
Moist N_2	- [2]	-	-	-	-	-	-	-	-
Moist Air	18.96	24.0	25.0	25.6	26.2	27.0	27.5	28.1	4.1
Moist N_2	10.17	24.0	30.9	34.7	35.9	36.7	37.1	37.3	13.3
Moist Air	10.17	24.0	28.6	32.1	34.4	35.8	36.5	37.2	13.2
Moist N_2	- [2]	-	-	-	-	-	-	-	-
Moist Air	4.20	24.0	37.6	45.2	49.5	50.8	51.8	52.6	28.6

1) Moisture saturated flow of Nitrogen (oxygen free) or Air at the rate of 200 ml/min.

2) These experiments are not included because of experimental difficulties which led to inconsistent results.

Table XIII

Temperature rise (°C) with varying equilibrium moisture deficiencies with selected coals when treated with DRY AIR.[1]

Coal Sample	Moisture (%)	Time (min.)							
		0	30	60	90	120	150	180	Total Rise(°C)
		Temperature (°C)							
Coal A	1.07	24.0	22.8	23.5	23.9	24.1	24.2	24.3	0.3
Low Valatile Bituminous	1.07	24.0	23.9	24.1	24.2	24.6	24.7	24.7	0.7
Equilibrium Moisture:	0.59	24.0	23.8	24.0	24.1	24.1	24.1	24.1	0.1
1.07%	0.84	24.0	24.4	24.4	24.5	24.5	24.6	24.6	0.6
Coal B	7.83	24.0	20.7	20.8	21.4	21.9	22.1.	22.3	-1.7
High Volatile Bituminous	7.08	24.0	21.1	21.3	21.8	22.2	22.4	22.6	-1.4
Equilibrium Moisture:	5.30	24.0	23.6	23.6	23.6	23.6	23.7	23.7	-0.3
7.83%	2.38	24.0	24.3	24.3	24.4	24.5	24.6	24.6	+0.6
Coal K	29.97	24.0	19.8	18.8	18.6	18.7	18.9	19.2	-4.8
(Lignite)	18.96	24.0	21.0	20.6	20.5	20.7	21.1	21.3	-2.7
Equilibrium Moisture:	10.17	24.0	22.8	22.6	23.0	23.4	23.5	23.6	-0.4
29.97%	8.15	24.0	23.2	23.3	23.4	23.7	23.8	23.9	-0.1

1) Flow rate of 200 ml/min.

Table XIV

Sequential gas flow experiment
Coal B - High Volatile Bituminous - Equilibrium moisture - 7.83%

Experimental Conditions[1,2]	Moisture (%)	Time (min.) 0	30	60	90	120	150	180	Total Rise(°C)
		Temperature (°C)							
Sample dried & treated with moist N_2	3.93	24.0	33.4	36.4	38.1	38.8	39.0	39.0	15.0
above treated sample redried & treated with moist N_2	3.81	24.0	31.5	35.1	37.1	37.8	38.0	38.1	14.1
above treated sample redried & treated with moist air	3.40	24.0	31.6	35.7	37.6	38.4	38.6	38.7	14.7
Sample dried & treated with moist air	2.91	24.0	35.4	40.1	42.4	43.3	43.6	43.7	19.7
above treated sample redired & treated with moist air	2.62	24.0	31.0	35.6	38.5	39.9	40.4	40.4	16.4
Sample dried & treated with moist air	2.75	24.0	36.0	41.4	43.8	44.7	44.9	44.9	20.9
above treated sample redried & treated with moist N_2	2.60	24.0	33.7	38.5	40.5	41.6	41.7	41.7	17.7

1) Moisture saturated Nitrogen (oxygen-free) or Air (RH ~97%)

2) Flow rate - 200 ml/min.

Table XV

Sequential gas flow experiment
Coal C - Subbituminous - Equilibrium moisture - 18.23%

Experimental Conditions[1,2]	Moisture (%)	Time (min.) 0	30	60	90	120	150	180	Total Rise(°C)
		Temperature (°C)							
Sample dried & treated with moist N_2	6.25	24.0	34.4	38.8	40.6	41.4	41.8	41.9	17.9
above treated sample redried & treated with moist N_2	6.05	24.0	30.9	35.0	37.3	38.3	38.8	39.2	15.2
above treated sample redried & treated with moist air	5.39	24.0	32.6	36.6	38.5	39.5	40.2	40.6	16.6
Sample dried & treated with moist air	4.61	24.0	35.5	42.1	45.3	47.0	47.6	47.8	23.8
above treated sample redired & treated with moist air	4.17	24.0	31.9	37.4	40.5	42.3	43.0	43.1	19.1
Sample dried & treated with moist air	4.10	24.0	36.0	41.1	43.8	45.8	46.6	47.1	23.1
above treated sample redried & treated with moist N_2	4.64	24.0	34.5	38.6	40.8	41.2	41.5	41.7	17.7

1) Moisture saturated Nitrogen (oxygen-free) or Air (RH ~97%)

2) Flow rate - 200 ml/min.

Table X"I

Sequential gas flow experiment
Coal D - Subbituminous - Equilibrium moisture - 20.55%

Experimental Conditions[1,2]	Moisture (%)	Time (min.)							
		0	30	60	90	120	150	180	Total Rise(°C)
		Temperature (°C)							
Sample dried & treated with moist N_2	6.98	24.0	33.0	37.6	40.0	41.0	41.2	41.2	17.2
above treated sample redried & treated with moist N_2	6.57	24.0	32.6	36.4	38.3	39.2	39.7	39.8	15.8
above treated sample redried & treated with moist air	5.73	24.0	32.0	36.7	39.1	40.4	41.1	41.7	17.7
Sample dried & treated with moist air	5.79	24.0	32.7	38.1	40.9	42.5	43.4	43.9	19.9
above treated sample redired & treated with moist air	5.20	24.0	32.0	35.8	38.9	40.5	41.4	41.8	17.8
Sample dried & treated with moist air	4.99	24.0	35.9	41.9	45.1	46.9	47.8	48.0	24.0
above treated sample redried & treated with moist N_2	4.49	24.0	33.5	38.0	40.8	41.8	42.6	42.8	18.8

1) Moisture saturated Nitrogen (oxygen-free) or Air (RH ~97%)

2) Flow rate - 200 ml/min.

Table XVII

Temperature rise (°C) with progressively drying High Volatile Bituminous Coal E when treated with Air Flow of varying moisture content.[1]
[Coal equilibrium moisture: 8.02%]

Experimental Conditions	Moisture (%)	Time (min.)							
		0	30	60	90	120	150	180	Total Rise(°C)
		Temperature (°C)							
Dry Air	7.91	21.0	18.2	18.2	18.2	18.3	18.4	18.9	-2.1
	4.75	21.0	20.2	19.9	19.9	20.0	20.1	20.2	-0.8
	3.27	21.0	20.7	20.6	20.6	20.6	20.6	20.6	-0.4
	2.82	21.0	20.9	20.8	20.8	20.8	20.8	20.8	-0.2
Moist Air (R.H. ~22%)	7.79	21.0	19.9	19.8	20.0	20.2	20.3	20.5	-0.5
	5.62	21.0	20.6	20.5	20.5	20.5	20.5	20.5	-0.5
	3.63	21.0	22.1	22.8	23.4	23.9	24.3	24.7	+3.7
	1.06	21.0	22.6	24.0	25.3	26.5	27.5	28.5	+7.5
Moist Air (R.H. ~60%)	8.02	21.0	20.6	20.9	21.1	21.4	21.6	21.8	0.8
	4.97	21.0	23.1	24.4	25.2	25.7	26.1	26.3	5.3
	2.86	21.0	25.7	28.4	30.7	32.1	33.1	33.7	12.7
	2.36	21.0	27.2	30.3	32.7	34.5	35.7	36.5	15.5
Moist Air (R.H. ~97%)	7.91	21.0	22.3	22.6	22.7	22.8	22.9	30.0	2.0
	4.63	21.0	26.3	29.6	31.7	33.1	33.7	33.9	12.9
	2.62	21.0	28.1	32.7	36.0	38.1	39.3	39.9	18.9
	1.92	21.0	27.7	32.7	36.4	39.1	41.2	41.8	20.8

1) Flow rate 150 ml/min.

Table XVIII

Temperature rise (°C) with progressively drying High Volatile Bituminous Coal F when treated with Air Flow of varying moisture content.[1]
[Coal equilibrium moisture: 8.36%]

Experimental Conditions	Moisture (%)	Time (min.)							
		0	30	60	90	120	150	180	Total Rise(°C)
		Temperature (°C)							
Dry Air	8.36	21.0	19.3	18.9	18.9	19.0	19.2	19.4	-1.6
	7.58	21.0	19.5	19.2	19.2	19.3	19.5	19.6	-1.4
	5.45	21.0	20.4	20.2	20.1	20.0	19.9	19.9	-1.1
	3.46	21.0	20.7	20.7	20.7	20.7	20.6	20.6	-0.4
Moist Air (R.H. ~22%)	8.22	21.0	19.4	19.3	19.5	19.7	19.8	20.0	-1.0
	6.04	21.0	20.9	20.7	20.5	20.5	20.3	20.3	-0.7
	3.64	21.0	23.3	24.0	24.5	24.9	25.2	25.5	+4.5
	1.07	21.0	23.0	24.5	26.0	27.3	28.4	29.3	+8.3
Moist Air (R.H. ~60%)	8.09	21.0	20.4	20.7	20.9	21.2	21.5	21.7	0.7
	4.89	21.0	23.0	24.4	25.7	26.5	27.2	27.7	6.7
	2.98	21.0	24.0	26.3	28.5	30.2	32.0	33.0	12.0
	2.33	21.0	24.6	27.3	29.8	32.1	33.9	35.5	14.5
Moist Air (R.H. ~97%)	8.11	21.0	21.9	22.3	22.4	22.5	22.5	22.6	1.6
	4.29	21.0	26.9	30.3	32.4	33.5	34.3	34.4	13.4
	3.20	21.0	27.5	31.9	34.9	36.8	37.9	38.4	17.4
	1.91	21.0	26.4	31.5	35.2	38.1	40.4	41.8	20.8

1) Flow rate 150 ml/min.

Table XIX

Temperature rise (°C) with progressively drying High Volatile Bituminous Coal G when treated with Air Flow of varying moisture content.[1]
[Coal equilibrium moisture: 8.21%]

Experimental Conditions	Moisture (%)	Time (min.)							
		0	30	60	90	120	150	180	Total Rise(°C)
		Temperature (°C)							
Dry Air	7.86	21.0	19.4	19.0	19.1	19.3	19.5	19.7	-1.3
	5.10	21.0	20.5	20.3	20.2	20.2	20.1	20.0	-1.0
	2.63	21.0	20.6	20.4	20.4	20.4	20.5	20.4	-0.6
Moist Air (R.H. ~22%)	7.67	21.0	19.4	19.3	19.3	19.3	19.5	19.6	-1.4
	5.52	21.0	21.0	20.9	20.8	20.8	20.6	20.5	-0.5
	3.39	21.0	21.8	22.6	23.2	23.7	24.2	24.6	+3.6
	0.89	21.0	23.4	25.6	27.1	28.5	29.6	30.5	+9.5
Moist Air (R.H. ~60%)	8.10	21.0	20.4	20.6	20.8	21.1	21.3	21.6	0.6
	4.07	21.0	23.3	25.0	26.5	27.6	28.5	29.3	8.3
	2.50	21.0	25.9	29.2	31.8	33.5	34.7	35.5	14.5
	2.38	21.0	24.9	28.2	31.0	33.2	34.9	36.1	15.1
Moist Air (R.H. ~97%)	8.21	21.0	21.8	22.0	22.2	22.3	22.4	22.5	1.5
	3.95	21.0	27.6	31.0	33.3	34.6	35.3	35.6	14.6
	2.82	21.0	25.8	29.8	33.7	36.1	37.6	38.5	17.5
	1.58	21.0	26.7	31.4	35.6	38.6	40.9	42.0	21.0

1) Flow rate 150 ml/min.

Table XX

Temperature rise (°C) with progressively drying High Volatile Bituminous Coal H when treated with Air Flow of varying moisture content.[1] [Coal equilibrium moisture: 11.65%].

Experimental Conditions	Moisture (%)	Time (min.)							
		0	30	60	90	120	150	180	Total Rise(°C)
		Temperature (°C)							
Dry Air	10.87	21.0	19.0	18.7	18.6	18.7	18.7	18.7	-2.3
	8.56	21.0	20.1	19.9	19.8	19.8	19.8	19.9	-1.1
	2.63	21.0	20.6	20.5	20.4	20.4	20.4	20.4	-0.6
	2.14	21.0	20.6	20.6	20.6	20.6	20.5	20.5	-0.5
Moist Air (R.H. ~22%)	11.65	21.0	19.9	19.6	19.6	19.7	19.8	19.9	-1.1
	8.41	21.0	20.7	20.5	20.4	20.3	20.2	20.0	-1.0
	4.86	21.0	21.7	22.4	23.0	23.4	23.8	24.1	+3.1
	1.60	21.0	22.5	23.8	25.1	26.3	27.3	28.5	+7.5
Moist Air (R.H. ~60%)	11.40	21.0	20.4	20.7	20.9	21.2	21.4	21.6	0.6
	7.62	21.0	22.5	23.2	23.6	24.0	24.3	24.4	3.4
	4.88	21.0	23.8	26.0	27.9	29.3	30.5	31.3	10.3
	3.07	21.0	25.5	28.3	30.7	32.4	33.9	34.9	13.9
Moist Air (R.H. ~97%)	11.62	21.0	21.3	21.6	22.1	22.2	22.4	22.5	1.5
	8.17	21.0	25.1	27.4	28.6	29.4	29.8	30.1	9.1
	5.73	21.0	26.9	30.6	33.5	35.1	36.2	36.8	15.8
	3.93	21.0	26.1	30.5	33.8	36.2	38.0	39.0	18.0
	2.76	21.0	26.9	31.6	35.6	39.0	41.3	42.5	21.5

1) Flow rate 150 ml/min.

Table XXI

Temperature rise (°C) with progressively drying High Volatile Bituminous Coal I when treated with Air Flow of varying moisture content.[1] [Coal equilibrium moisture: 12.51%].

Experimental Conditions	Moisture (%)	Time (min.)							
		0	30	60	90	120	150	180	Total Rise(°C)
		Temperature (°C)							
Dry Air	12.41	21.0	18.5	18.3	18.3	18.4	18.5	18.6	-2.4
	11.76	21.0	19.3	18.7	18.7	18.7	18.8	19.1	-1.9
	9.14	21.0	20.1	19.9	19.8	19.8	19.8	19.9	-1.1
	3.94	21.0	20.6	20.4	20.3	20.3	20.3	20.2	-0.8
	2.11	21.0	20.7	20.6	20.5	20.5	20.5	20.5	-0.5
Moist Air (R.H. ~22%)	12.51	21.0	19.6	19.3	19.2	19.3	19.4	19.4	-1.6
	8.78	21.0	21.2	21.2	21.1	21.1	21.1	21.1	+0.1
	4.79	21.0	21.9	22.6	23.2	23.7	24.1	24.5	+3.5
	1.58	21.0	22.7	24.0	25.3	26.5	27.6	28.6	+7.6
Moist Air (R.H. ~60%)	11.96	21.0	20.5	20.7	20.9	21.2	21.4	21.7	0.7
	8.55	21.0	22.8	23.8	24.4	24.9	25.1	25.2	4.2
	4.41	21.0	23.7	25.9	27.7	29.2	30.4	31.6	10.6
	2.92	21.0	24.2	26.9	29.2	31.0	32.5	33.8	12.8
Moist Air (R.H. ~97%)	12.40	21.0	22.6	22.8	22.9	23.0	23.1	23.2	2.2
	8.29	21.0	25.1	27.2	28.5	29.2	29.7	29.9	8.9
	3.70	21.0	26.6	30.8	34.7	37.8	39.7	40.8	19.8
	2.24	21.0	26.6	31.4	35.9	39.4	42.2	43.9	22.9

1) Flow rate 150 ml/min.

Table XXII

Temperature rise (°C) with progressively drying Subbituminous Coal J when treated with Air Flow of varying moisture content.[1] [Coal equilibrium moisture: 19.49%].

Experimental Conditions	Moisture (%)	Time (min.)							
		0	30	60	90	120	150	180	Total Rise(°C)
		Temperature (°C)							
Dry Air	19.29	21.0	18.6	18.3	18.3	18.3	18.4	18.6	-2.4
	14.37	21.0	19.9	19.5	19.4	19.4	19.3	19.2	-1.8
	5.82	21.0	20.7	20.4	20.2	20.0	19.9	19.9	-1.1
Moist Air (R.H. ~22%)	19.24	21.0	20.1	19.8	19.6	19.4	19.5	19.6	-1.4
	13.66	21.0	20.7	20.6	20.6	20.6	20.6	20.7	-0.3
	6.34	21.0	22.0	22.7	23.3	23.8	24.3	24.6	+3.6
	2.55	21.0	22.4	23.7	24.8	25.8	26.7	27.6	+6.6
Moist Air (R.H. ~60%)	18.89	21.0	20.4	20.5	20.6	20.8	21.0	21.1	0.1
	13.25	21.0	22.1	22.9	23.4	23.7	24.0	24.2	3.2
	5.98	21.0	24.2	26.6	28.6	30.2	31.7	32.5	11.5
	3.43	21.0	26.8	30.5	32.9	35.0	36.3	37.3	16.3
Moist Air (R.H. ~97%)	19.49	21.0	21.3	21.5	21.7	21.8	22.0	22.2	1.2
	12.70	21.0	23.7	26.0	27.5	28.7	29.3	29.7	8.7
	5.32	21.0	26.2	30.0	33.7	36.0	37.8	39.1	18.1
	3.37	21.0	26.2	30.5	34.0	37.1	39.5	41.9	20.9

1) Flow rate 150 ml/min.

Table XXIII

Peroxygen analyses of different ranks of coal

Sample	Rank	Equilibrium moisture content	Peroxygen g/g
Coal-A	lvb	1.07%	0.15×10^{-5}
Coal-B	hvb	7.83%	1.43×10^{-5}
Coal-C	sub	18.23%	2.39×10^{-5}
Coal-D	sub	20.55%	4.47×10^{-5}
Coal-E	hvb	8.02%	2.22×10^{-5}
Coal-F	hvb	8.36%	1.87×10^{-5}
Coal-G	hvb	8.21%	2.75×10^{-5}
Coal-H	hvb	11.65%	1.85×10^{-5}
Coal-I	hvb	12.51%	1.66×10^{-5}
Coal-J	sub	19.49%	4.97×10^{-5}
Coal-K	lig	29.97%	6.51×10^{-5}

Table XXIV
Peroxygen analyses of treated coal samples in the sequential gas-flow analyses experiments.

Coal Sample	Rank	Treatment	Peroxygen g/g coal
Coal-B	hvb	a) equilibrated coal (at ~97% R.H.)	2.64×10^{-5}
		b) a)-dried (in vac/P_2O_5)	2.20×10^{-5}
		c) b) treated with moisture saturated O_2 free N_2	2.37×10^{-5}
		d) c) redried (vac/P_2O_5) and treated with moisture saturated O_2 free N_2	2.68×10^{-5}
		e) d) redried (vac/P_2O_5) and treated with moisture saturated air	2.72×10^{-5}
		f) b) treated with moisture saturated air	2.52×10^{-5}
Coal-C	sub	a) equilibrated coal (at ~97% R.H.)	N.A.
		b) a)-dried (in vac/P_2O_5)	5.97×10^{-5}
		c) b) treated with moisture saturated O_2 free N_2	6.05×10^{-5}
		d) c) redried (vac/P_2O_5) and treated with moisture saturated O_2 free N_2	6.57×10^{-5}
		e) d) redried (vac/P_2O_5) and treated with moisture saturated air	6.09×10^{-5}
		f) b) treated with moisture saturated	6.04×10^{-5}
Coal-D	sub	a) equilibrated coal (at ~97% R.H.)	NA
		b) a)-dried (in vac/P_2O_5)	6.57×10^{-5}
		c) b) treated with moisture saturated O_2 free N_2	6.75×10^{-5}
		d) c) redried (vac/P_2O_5) and treated with moisture saturated O_2 free N_2	7.24×10^{-5}
		e) d) redried (vac/P_2O_5) and treated with moisture saturated air	6.28×10^{-5}
		f) b) treated with moisture saturated	6.37×10^{-5}

Table XXV

Peroxygen analyses of moisture equilibrated coal samples
(AIR treated)

Coal Sample	Rank	Initial	Peroxygen g/g Coal			
			Treated with AIR-flow of varying rel. humidities			
			~97%	~60%	~22%	dry
Coal-E	hvb	2.22×10^{-5}	2.19×10^{-5}	1.91×10^{-5}	2.15×10^{-5}	2.26×10^{-5}
Coal-F	hvb	1.87×10^{-5}	1.87×10^{-5}	1.56×10^{-5}	1.55×10^{-5}	1.97×10^{-5}
Coal-G	hvb	2.75×10^{-5}	2.75×10^{-5}	2.12×10^{-5}	2.01×10^{-5}	2.60×10^{-5}
Coal-H	hvb	1.85×10^{-5}	2.00×10^{-5}	1.87×10^{-5}	1.86×10^{-5}	2.43×10^{-5}
Coal-I	hvb	1.66×10^{-5}	1.67×10^{-5}	1.70×10^{-5}	1.80×10^{-5}	1.85×10^{-5}
Coal-J	sub	4.97×10^{-5}	5.10×10^{-5}	4.72×10^{-5}	5.63×10^{-5}	5.77×10^{-5}

Table XXVI

Peroxygen analyses of dried (vac/P_2O_5) coal samples
(AIR treated)

Coal Sample	Rank	Peroxygen g/g Coal				
			Treated with AIR-flow of varying rel. humidities			
		Initial	~97%	~60%	~22%	dry
Coal-E	hvb	1.79×10^{-5}	1.87×10^{-5}	2.16×10^{-5}	2.21×10^{-5}	1.95×10^{-5}
Coal-F	hvb	1.31×10^{-5}	1.51×10^{-5}	1.48×10^{-5}	1.66×10^{-5}	1.81×10^{-5}
Coal-G	hvb	1.52×10^{-5}	1.56×10^{-5}	1.90×10^{-5}	2.24×10^{-5}	1.94×10^{-5}
Coal-H	hvb	1.84×10^{-5}	1.67×10^{-5}	1.98×10^{-5}	2.00×10^{-5}	2.05×10^{-5}
Coal-I	hvb	1.62×10^{-5}	1.57×10^{-5}	1.51×10^{-5}	1.72×10^{-5}	1.85×10^{-5}
Coal-J	sub	5.08×10^{-5}	5.71×10^{-5}	5.90×10^{-5}	5.26×10^{-5}	5.85×10^{-5}

Table XXVII

E.P.R. study

Rank Factor

	Low Volatile Bituminous	High Volatile Bituminous	Subbituminous		Lignite
Parameters	Coal A	Coal B	Coal C	Coal D	Coal K
g factor	2.0022(7)	2.0024(9)	2.0026(3)	2.0027(7)	2.0029(9)
Area	236095.25	9268.915	6955.121	6059.718	2537.418
ΔH_{pp} (Linewidth - peak to peak)	4.732770	6.259470	5.496120	6.870150	7.175490
$\Delta H_{1/2}$ (Half-line width)	8.296853	9.705702	8.900623	10.24382	10.39742
$A/(Y_m \Delta H_{1/2})$	1.289730	1.247728	1.272786	1.284588	1.263695
$A/(Y'_m \Delta H_{1/2})$	3.133197	2.311356	2.609814	2.161972	2.024101
$\langle H^2 \rangle / (\Delta H_{1/2})^2$	0.6258843	0.5381480	0.6129544	0.6049585	0.5581030
$\langle H^4 \rangle / (\Delta H_{1/2})^4$	2.556412	1.809431	2.488014	2.134590	1.865132
$\langle H^2 \rangle / (\Delta H_{pp})^2$	1.923491	1.293840	1.607521	1.344983	1.171825
$\langle H^4 \rangle / (\Delta H_{pp})^4$	24.14477	10.45923	17.11235	10.55109	8.222537
$\langle H^2 \rangle$	1848.475	2174.945	2083.347	2723.591	2588.560
$\langle H^4 \rangle \times 10^7$	2.2298198	2.9555276	2.8742172	4.3266052	4.0123360

A = Area.

Y_m = Maximum absorption amplitude.

Y'_m = Maximum first derivative amplitude.

$\langle H^2 \rangle$ = 2nd moment of the resonance absorption.

$\langle H^4 \rangle$ = 4th moment of the resonance absorption.

Table XXVIII
E.P.R. Study (Coal B)
Moisture/Oxidation Study

Parameters	equilib-rated at ~97%	Sample dried under vac. over P_2O_5	Sample (dried) treated with moist Nitrogen (X)	(X) redried treated with moist air (Y)	(Y) redried treated with moist air	Sample (dried) treated with moist air
g factor	2.0024(9)	2.0028(5)	2.0025(6)	2.0024(3)	2.0024(9)	2.0022(0)
Area	9268.915	10178.227	10403.42	10644.371	9916.989	9575.732
ΔH_{pp} (Linewidth-peak to peak)	6.259470	6.259470	6.259470	6.412140	6.106800	6.259470
$\Delta H_{1/2}$ (Half-line width)	9.705702	9.884106	9.758840	9.753927	9.752090	9.767272
$A/(Y_m \Delta H_{1/2})$	1.247728	1.234168	1.241140	1.242202	1.240537	1.193503
$A/(Y'_m \Delta H_{1/2})$	2.311356	2.672750	2.360679	2.234459	2.432691	1.959437
$\langle H^2 \rangle/(\Delta H_{1/2})^2$	0.5381480	0.4832721	0.5220905	0.5228160	0.5121167	0.2486847
$\langle H^4 \rangle/(\Delta H_{1/2})^4$	1.809431	1.132088	1.717659	1.704627	1.573998	1.623762
$\langle H^2 \rangle/(\Delta H_{pp})^2$	1.293840	1.205012	1.269016	1.209768	1.305981	0.6055088
$\langle H^4 \rangle/(\Delta H_{pp})^4$	10.45923	7.038486	10.14798	9.127157	10.23624	9.626429
$\langle H^2 \rangle$	2174.945	2025.625	2133.216	2134.030	2089.570	1017.860
$\langle H^4 \rangle \times 10^7$	2.9555276	1.9889080	2.8675760	2.8400940	2.6204772	2.7201986

A = Area.

Y_m = Maximum absorption amplitude.

Y'_m = Maximum first derivative amplitude.

$\langle H^2 \rangle$ = 2nd moment of the resonance absorption.

$\langle H^4 \rangle$ = 4th moment of the resonance absorption.

Table XXIX
E.P.R. Study (Coal C)
Moisture/Oxidation Study

Parameters	equilib-rated at ~97%	Sample dried under vac. over P_2O_5	Sample (dried) treated with moist Nitrogen (X)	(X) redried treated with moist Nitrogen (Y)	(Y) redried treated with moist air	Sample (dried) treated with moist air
g factor	2.0026(3)	2.0026(1)	2.0025(9)	2.0024(5)	2.0026(5)	2.0023(0)
Area	6955.121	10951.885	9473.398	9357.363	10694.507	9938.503
ΔH_{pp} (Linewidth - peak to peak)	5.496120	5.648790	5.648790	5.496120	5.648790	5.496120
$\Delta H_{1/2}$ (Half-line width)	8.900623	9.270252	9.168521	9.152714	9.189962	9.225979
$A/(Y_m \Delta H_{1/2})$	1.272786	1.270196	1.274175	1.262138	1.275342	1.226619
$A/(Y'_m \Delta H_{1/2})$	2.609814	2.694913	2.672825	2.622787	2.744688	2.381022
$\langle H^2 \rangle / (\Delta H_{1/2})^2$	0.6129544	0.5920928	0.6081597	0.5474690	0.6191999	0.3281761
$\langle H^4 \rangle / (H_{1/2})^4$	2.488014	2.202280	2.375857	1.606581	2.515142	1.383682
$\langle H^2 \rangle / (\Delta H_{pp})^2$	1.607521	1.594638	1.602158	1.518263	1.638882	0.9247398
$\langle H^4 \rangle / (\Delta H_{pp})^4$	17.11235	15.97413	16.48905	12.35599	17.61960	10.98655
$\langle H^2 \rangle$	2083.347	2183.059	2193.354	1967.668	2243.629	1198.463
$\langle H^4 \rangle \times 10^7$	2.8742172	2.9938086	3.0903142	2.0753312	3.3021960	1.8453186

A = Area.

Y_m = Maximum absorption amplitude.

Y'_m = Maximum first derivative amplitude.

$\langle H^2 \rangle$ = 2nd moment of the resonance absorption.

$\langle H^4 \rangle$ = 4th moment of the resonance absorption.

Table XXX
E.P.R. Study (Coal D)
Moisture/Oxidation Study

Parameters	equilib-rated at ~97%	Sample dried under vac. over P_2O_5	Sample (dried) treated with moist Nitrogen (X)	(X) redried treated with moist air (Y)	(Y) redried treated with moist air	Sample (dried) treated with moist air
g factor	2.0027(7)	2.0028(3)	2.0027(6)	2.0023(6)	2.0028(1)	2.0027(2)
Area	6059.718	9027.573	8161.616	7583.821	8525.978	8544.401
ΔH_{pp} (Linewidth - peak to peak)	6.870150	6.717480	7.175490	7.022820	6.870150	6.870150
$\Delta H_{1/2}$ (Half-line width)	10.24382	10.70736	10.68791	10.66168	10.71947	10.72377
$A/(Y_m \Delta H_{1/2})$	1.284588	1.278009	1.278265	1.233765	1.280652	1.275477
$A/(Y'_m \Delta H_{1/2})$	2.161972	2.532420	2.155341	1.920289	2.391590	2.305604
$\langle H^2 \rangle/(\Delta H_{1/2})^2$	0.6049585	0.5752131	0.5736828	0.3956883	0.5812646	0.5649638
$\langle H^4 \rangle/(\Delta H_{1/2})^4$	2.134590	1.867081	1.843411	0.1730752	1.893759	1.764635
$\langle H^2 \rangle/(\Delta H_{pp})^2$	1.344983	1.461441	1.272783	0.9119717	1.415104	1.376521
$\langle H^4 \rangle/(\Delta H_{pp})^4$	10.55109	12.05224	9.073758	0.9193716-	11.22416	10.47561
$\langle H^2 \rangle$	2723.591	2829.349	2811.577	1929.732 .	2865.586	2787.455
$\langle H^4 \rangle \times 10^7$	4.3266052	4.5172960	4.4277044	0.4116446-	4.6026052	4.2956564

A = Area.

Y_m = Maximum absorption amplitude.

Y'_m = Maximum first derivative amplitude.

$\langle H^2 \rangle$ = 2nd moment of the resonance absorption.

$\langle H^4 \rangle$ = 4th moment of the resonance absorption.

Appendix III - Figures

FIGURE 8

TEMPERATURE RESPONSE OF COAL-A TO GAS FLOW
OXYGEN FREE NITROGEN - R.H. 97%

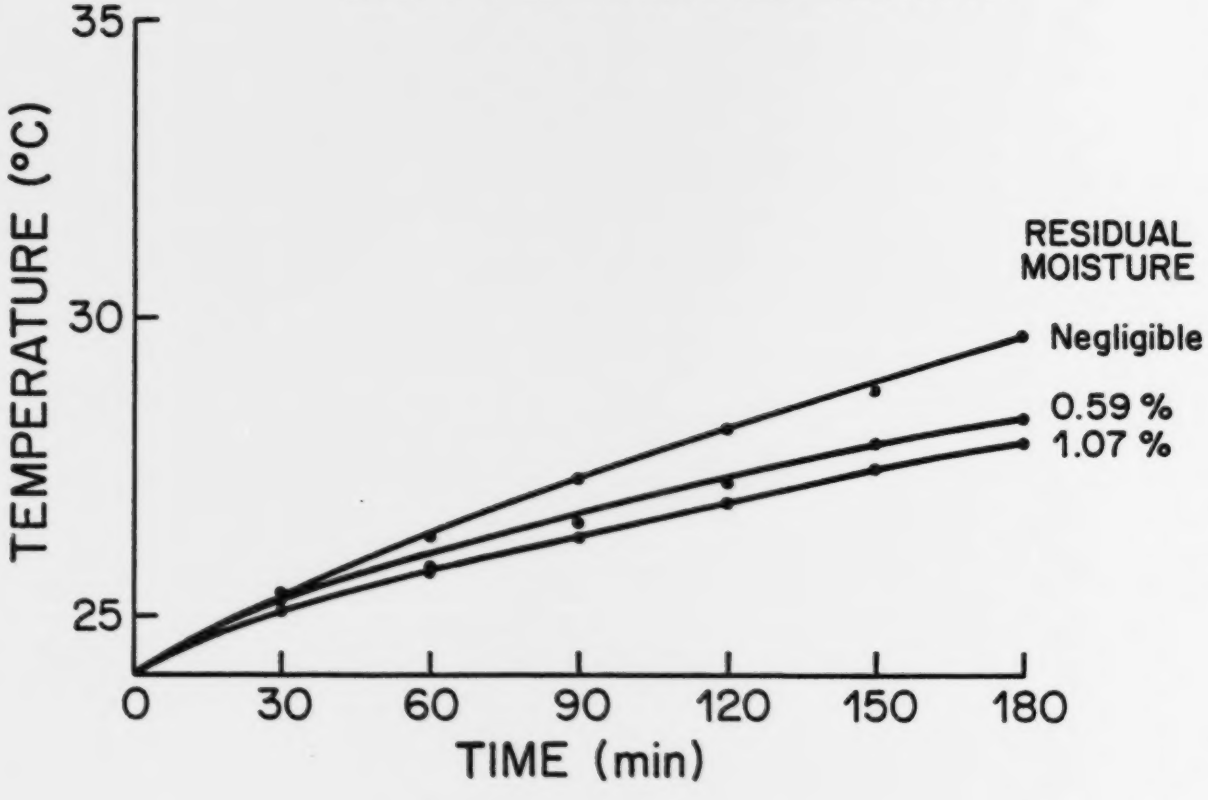


FIGURE 9

TEMPERATURE RESPONSE OF COAL-B TO GAS FLOW
OXYGEN FREE NITROGEN - R.H. 97%

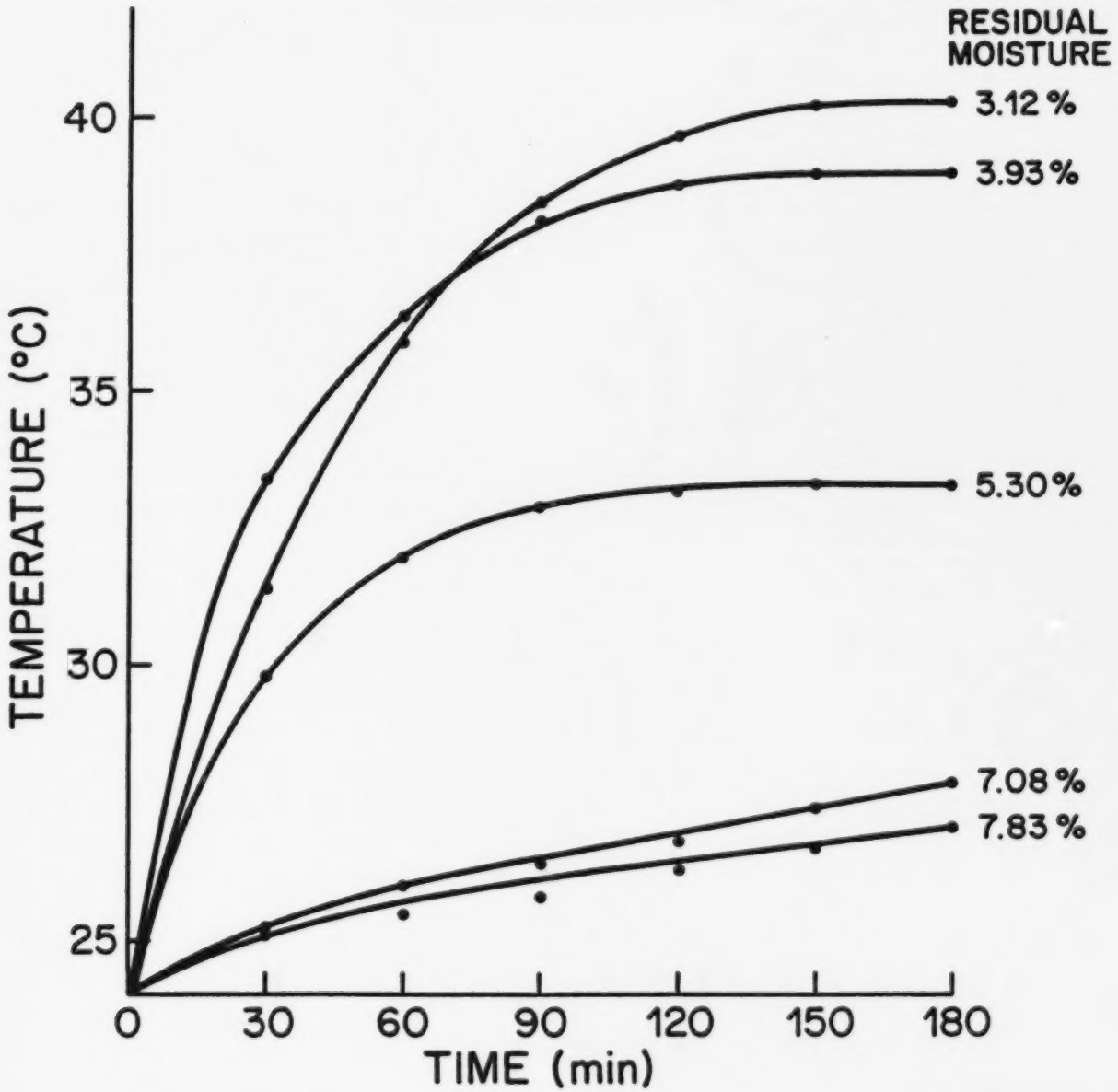


FIGURE 10

TEMPERATURE RESPONSE OF COAL-C TO GAS FLOW
OXYGEN FREE NITROGEN - R.H. 97%

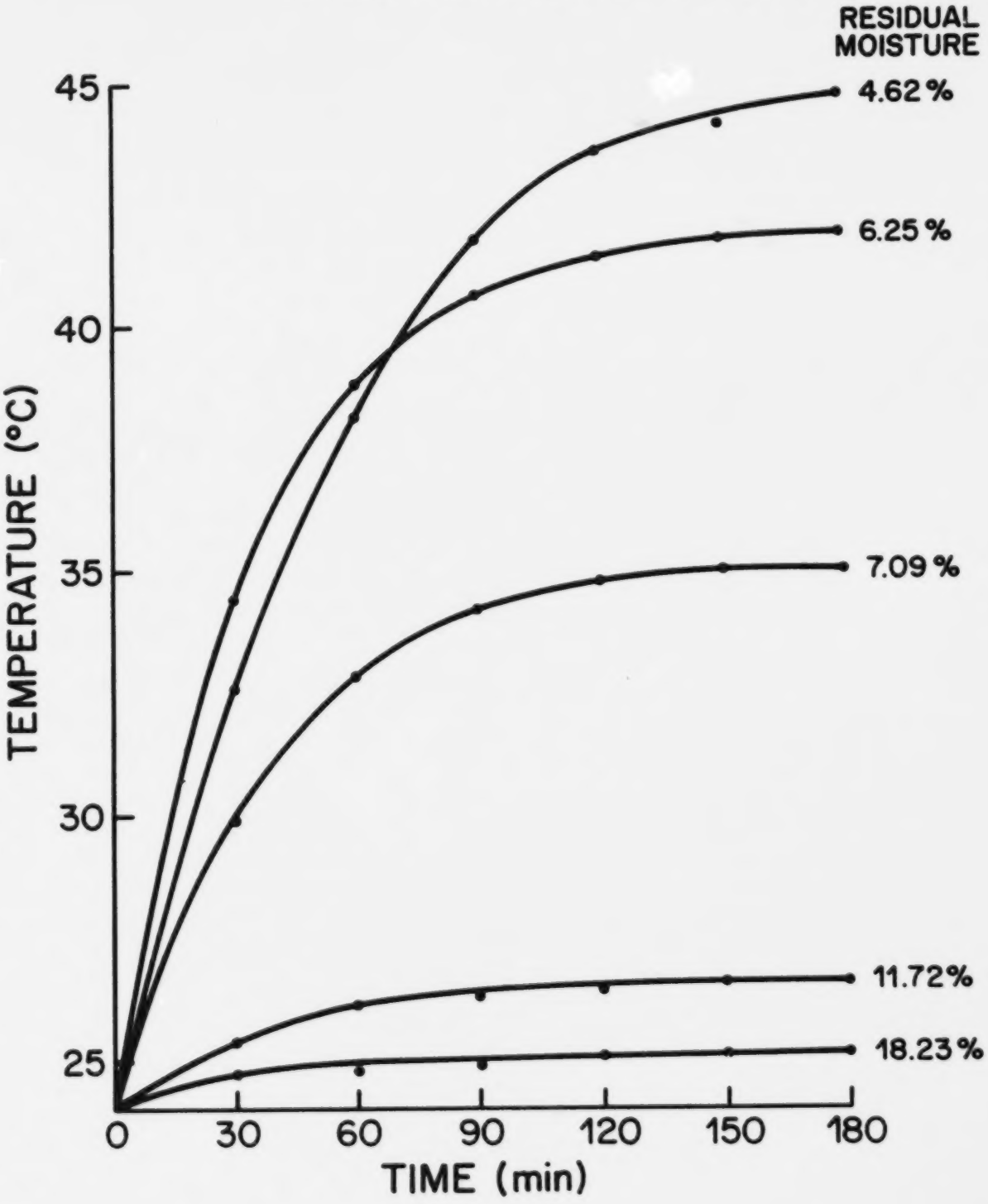


FIGURE 11

TEMPERATURE RESPONSE OF COAL-D TO GAS FLOW
OXYGEN FREE NITROGEN - R.H. 97%

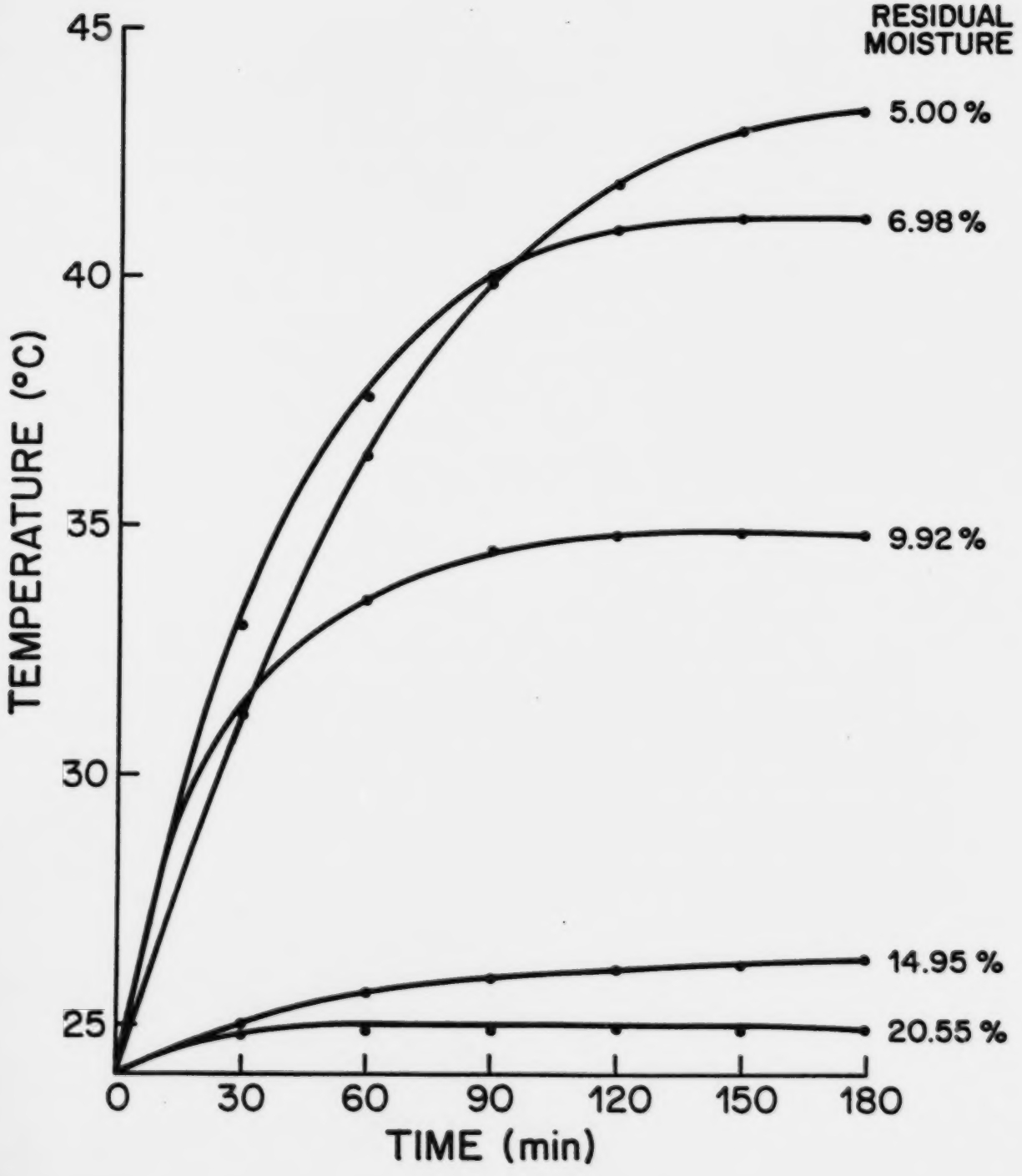


FIGURE 12

TEMPERATURE RESPONSE OF COAL-SAMPLES TO GAS FLOW
OXYGEN FREE NITROGEN - R.H. 97%

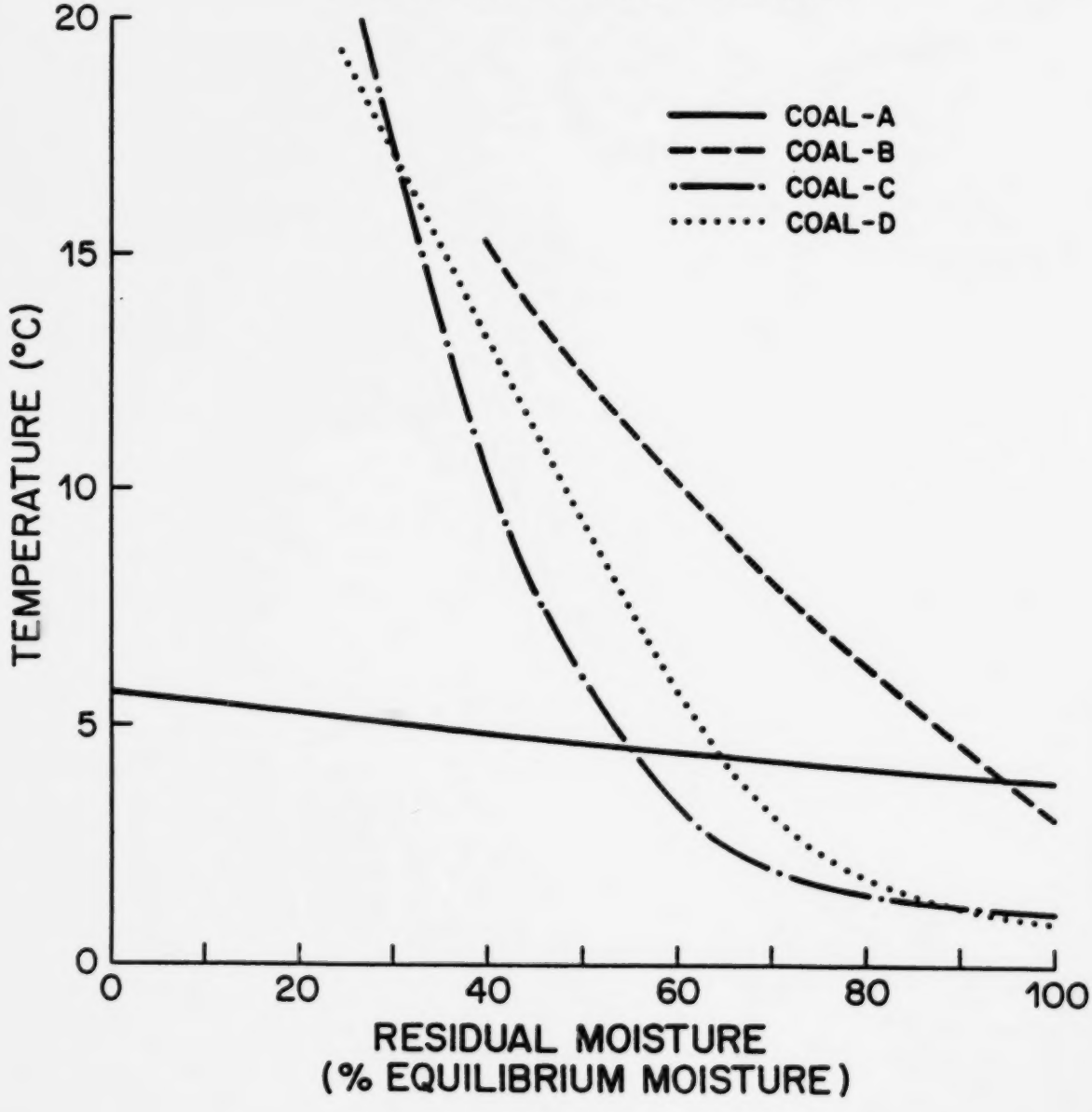


FIGURE 13

TEMPERATURE RESPONSE OF COAL-A TO GAS FLOW
AIR - R.H. 97%

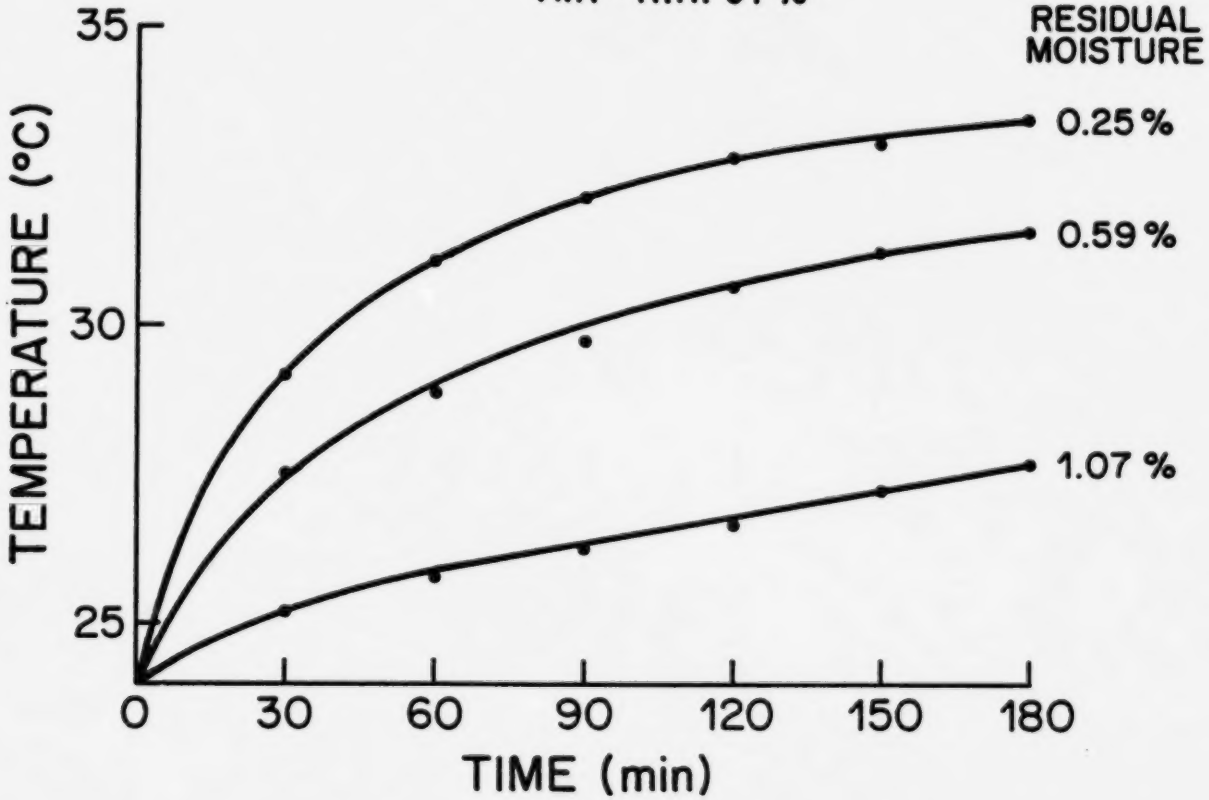


FIGURE 14

TEMPERATURE RESPONSE OF COAL-B TO GAS FLOW
AIR - R.H. 97%

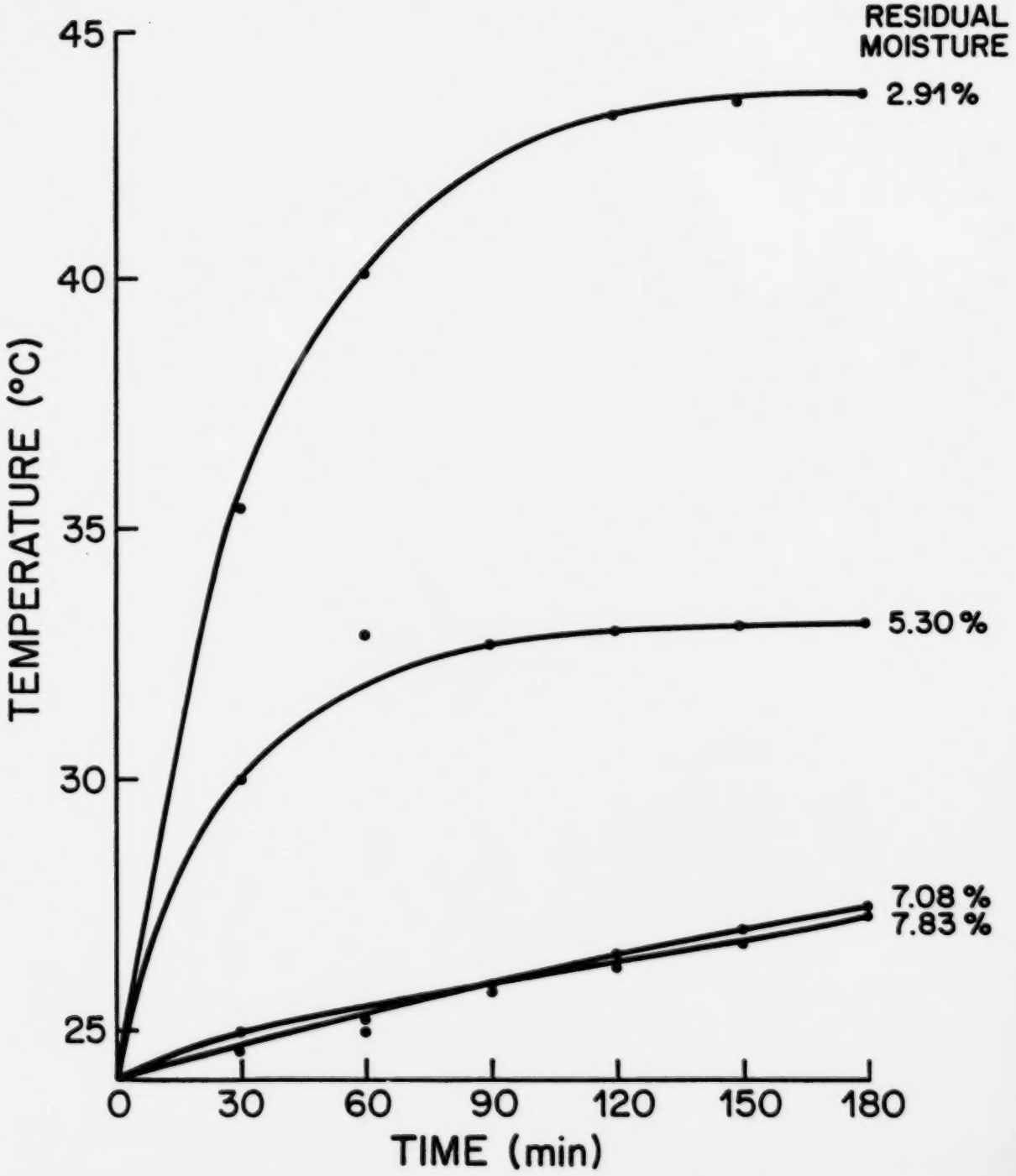


FIGURE 15

TEMPERATURE RESPONSE OF COAL-C TO GAS FLOW
AIR - R.H. 97%

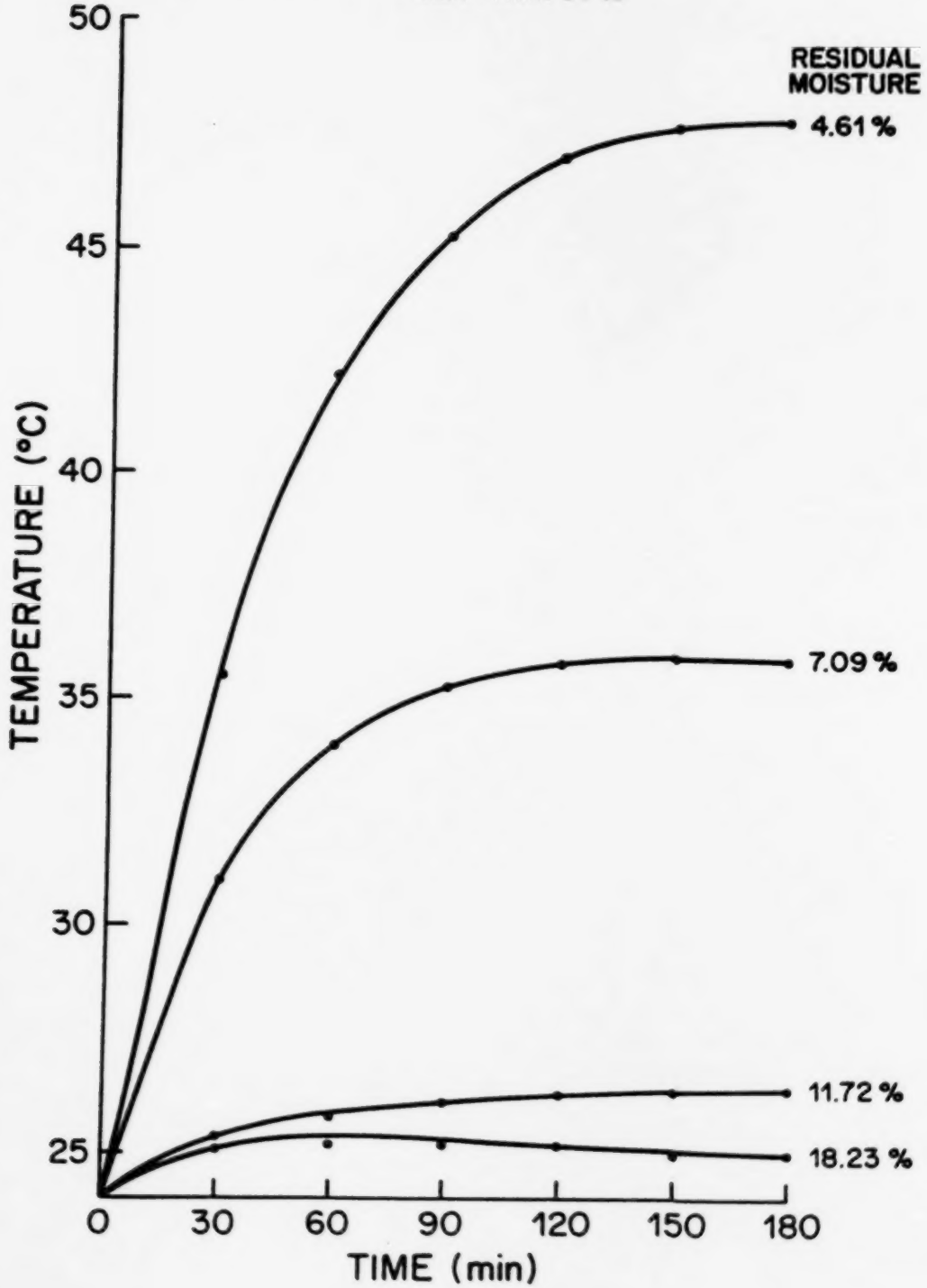


FIGURE 16

TEMPERATURE RESPONSE OF COAL-D TO GAS FLOW
AIR - R.H. 97%

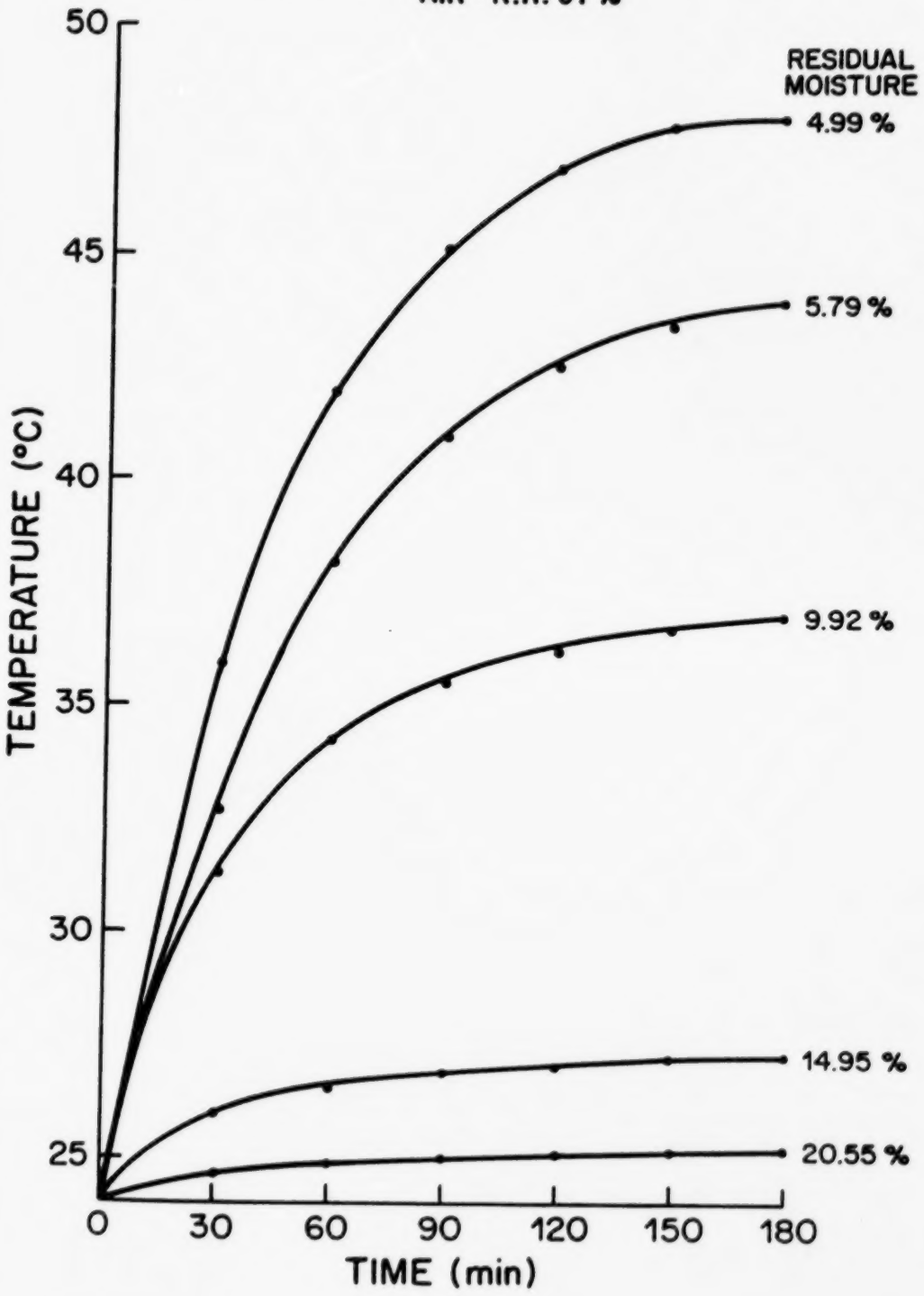


FIGURE 17

TEMPERATURE RESPONSE OF COAL-K TO GAS FLOW
AIR - R.H. 97%

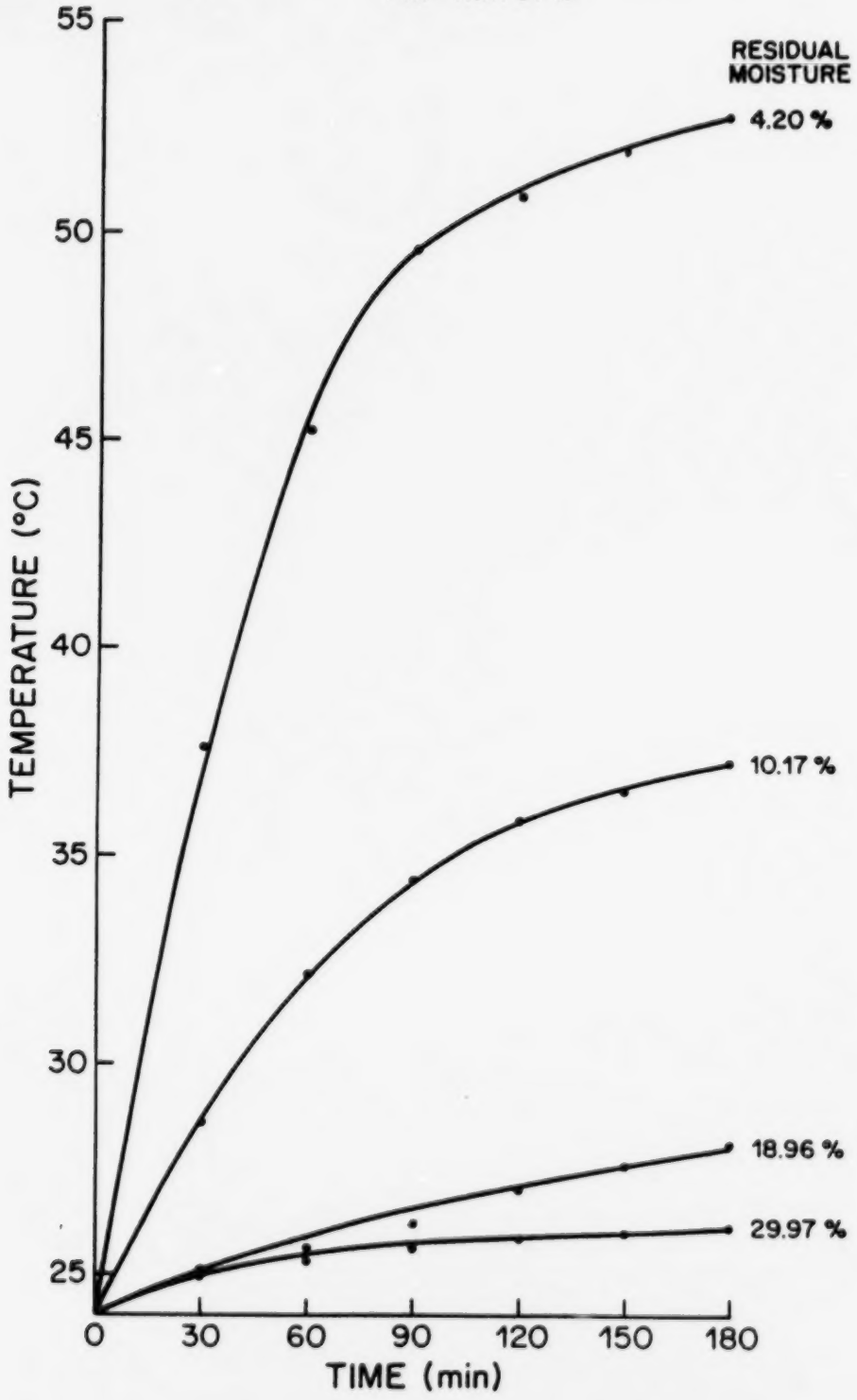


FIGURE 18

TEMPERATURE RESPONSE OF COAL-SAMPLES TO GAS FLOW
AIR - R.H. 97%

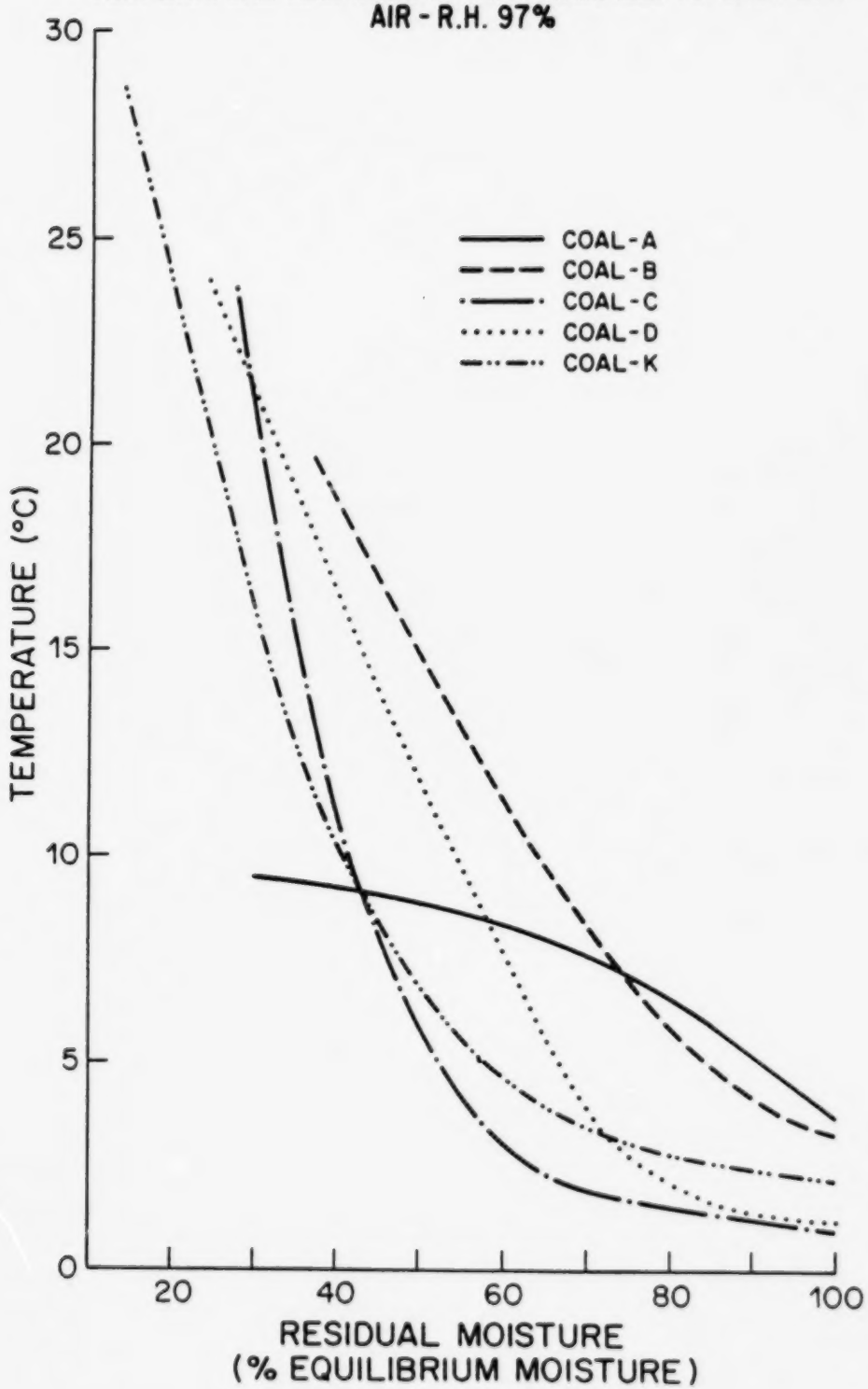


FIGURE 19

TEMPERATURE RESPONSE OF COAL-E TO GAS FLOW
AIR-DRY

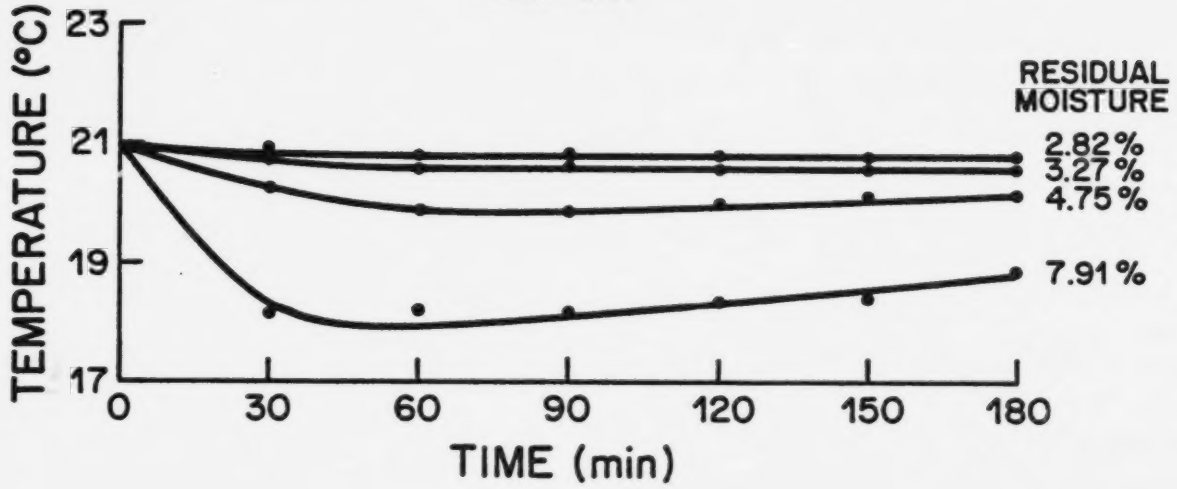


FIGURE 20

TEMPERATURE RESPONSE OF COAL-F TO GAS FLOW
AIR-DRY

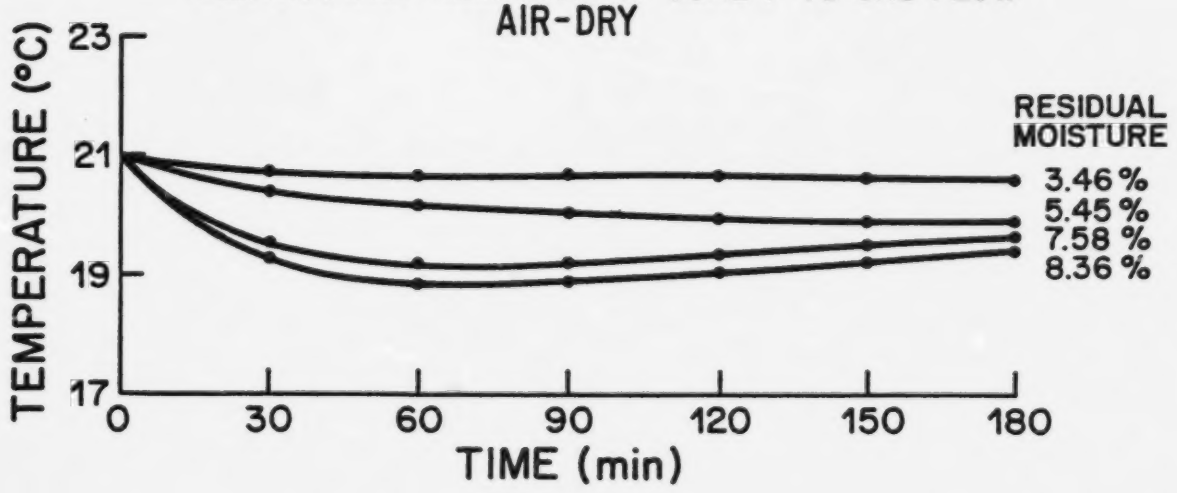


FIGURE 21

TEMPERATURE RESPONSE OF COAL-G TO GAS FLOW
AIR-DRY

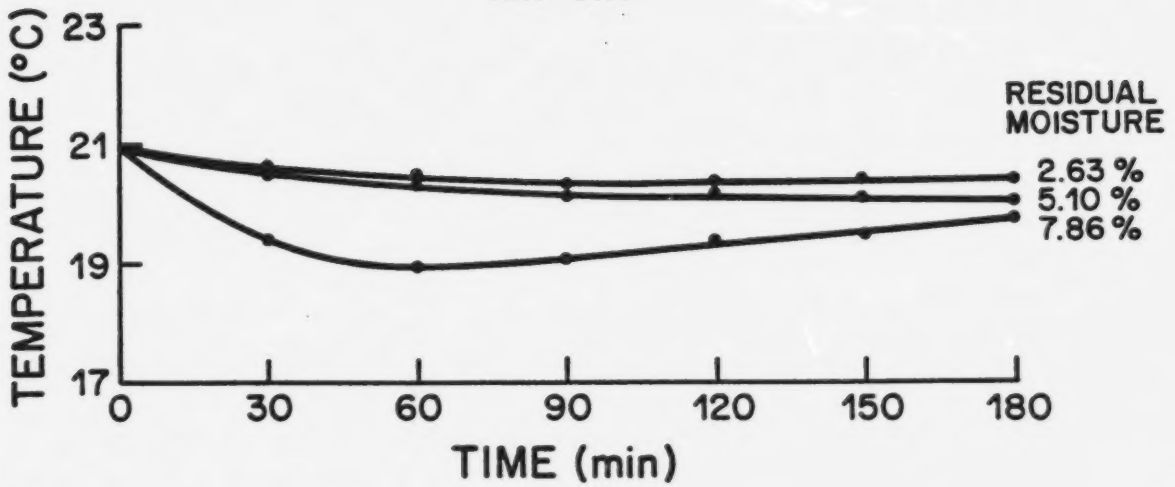


FIGURE 22

TEMPERATURE RESPONSE OF COAL-H TO GAS FLOW
AIR-DRY

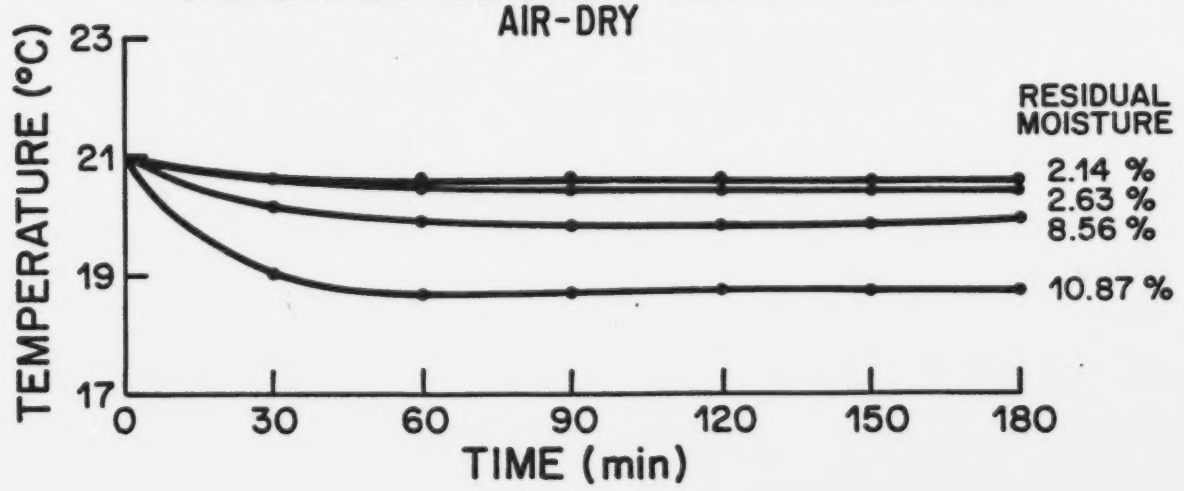


FIGURE 23

TEMPERATURE RESPONSE OF COAL-I TO GAS FLOW
AIR-DRY

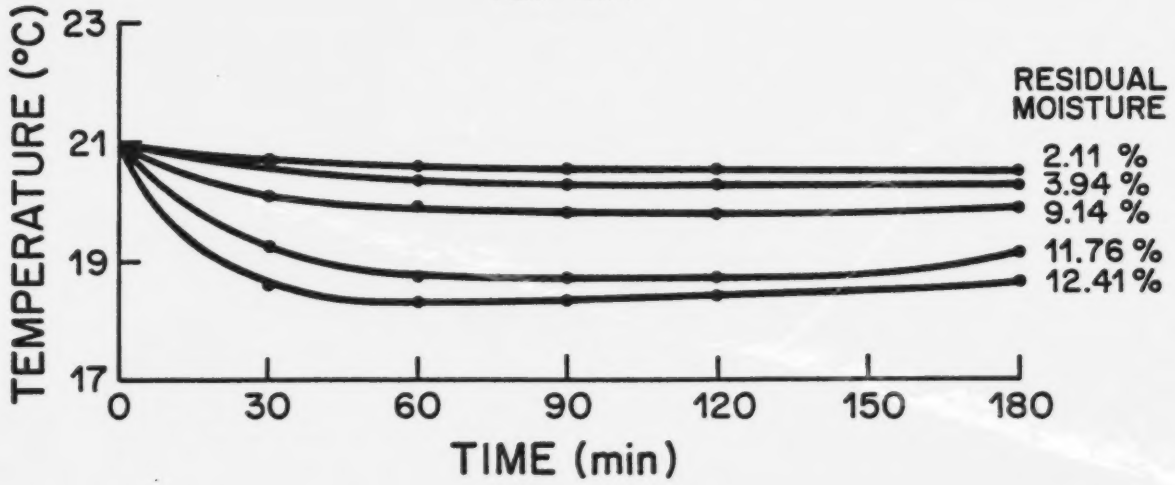


FIGURE 24

TEMPERATURE RESPONSE OF COAL-J TO GAS FLOW
AIR-DRY

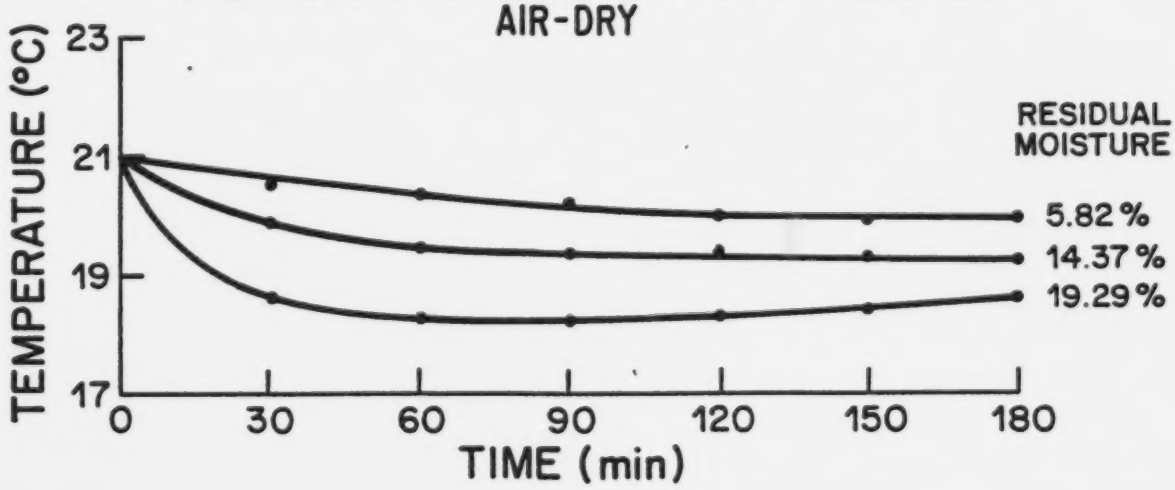


FIGURE 25

TEMPERATURE RESPONSE OF COAL-E TO GAS FLOW
AIR - R.H. 22%

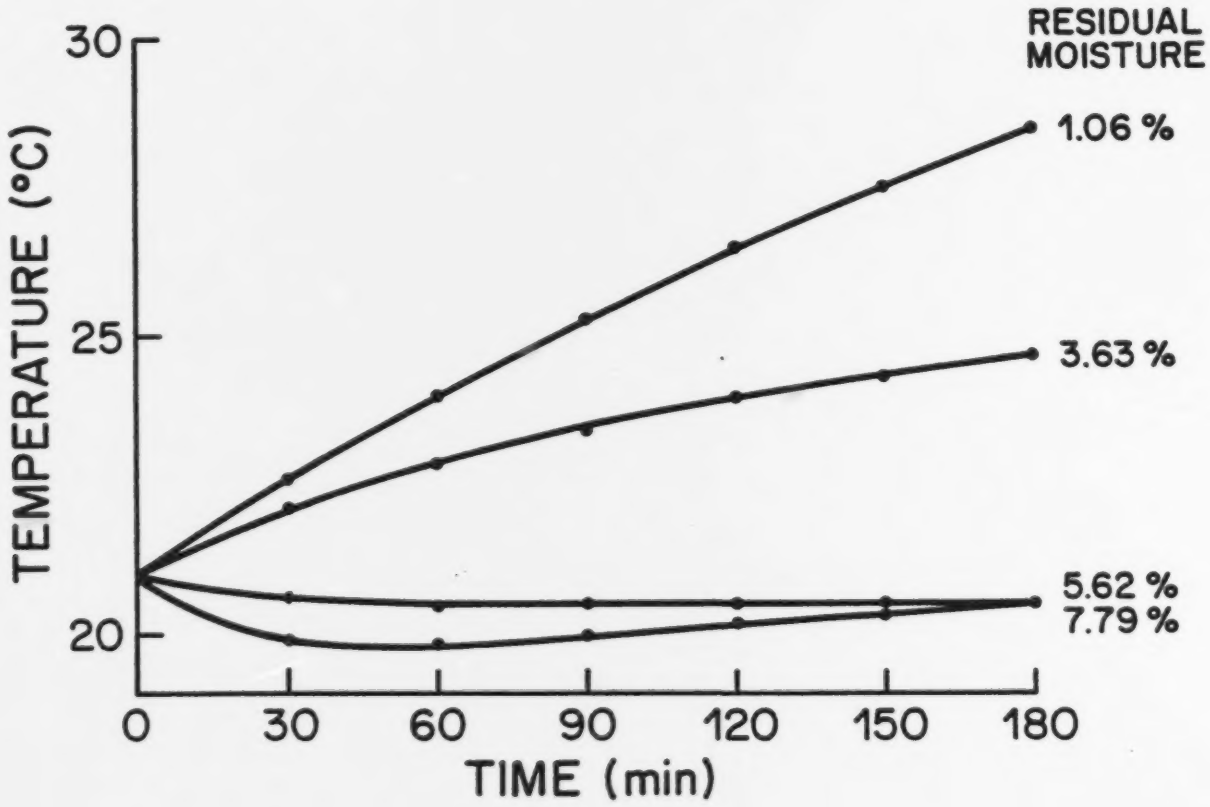


FIGURE 26

TEMPERATURE RESPONSE OF COAL-F TO GAS FLOW
AIR - R.H. 22%

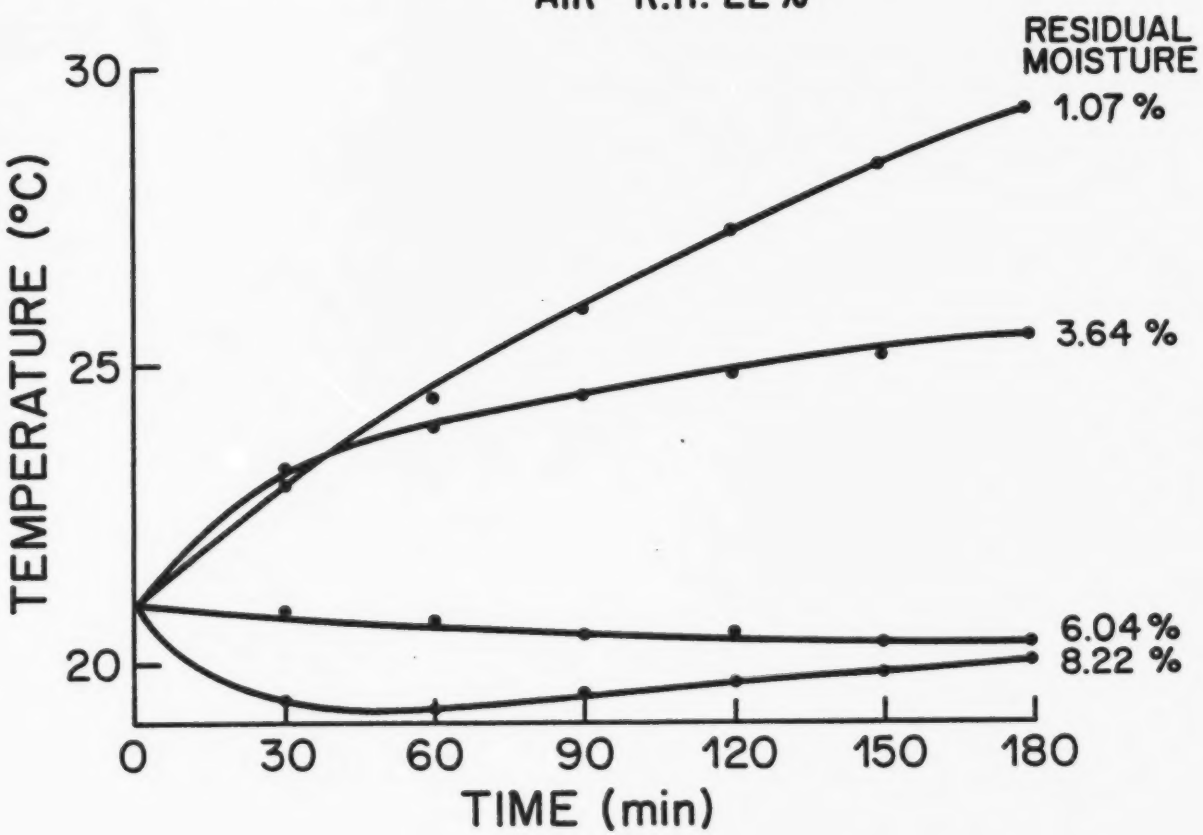


FIGURE 27

TEMPERATURE RESPONSE OF COAL-G TO GAS FLOW
AIR - R.H. 22%

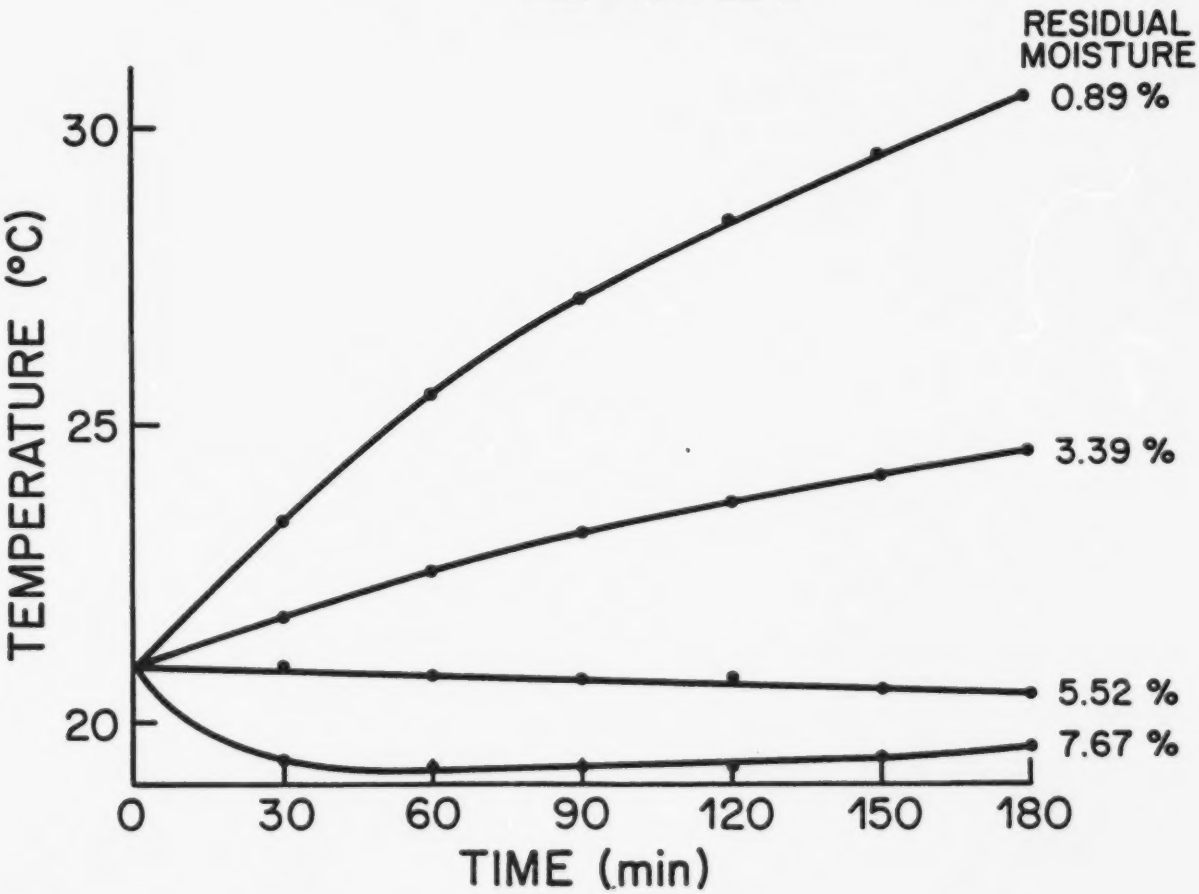


FIGURE 28

TEMPERATURE RESPONSE OF COAL-H TO GAS FLOW
AIR - R.H. 22%

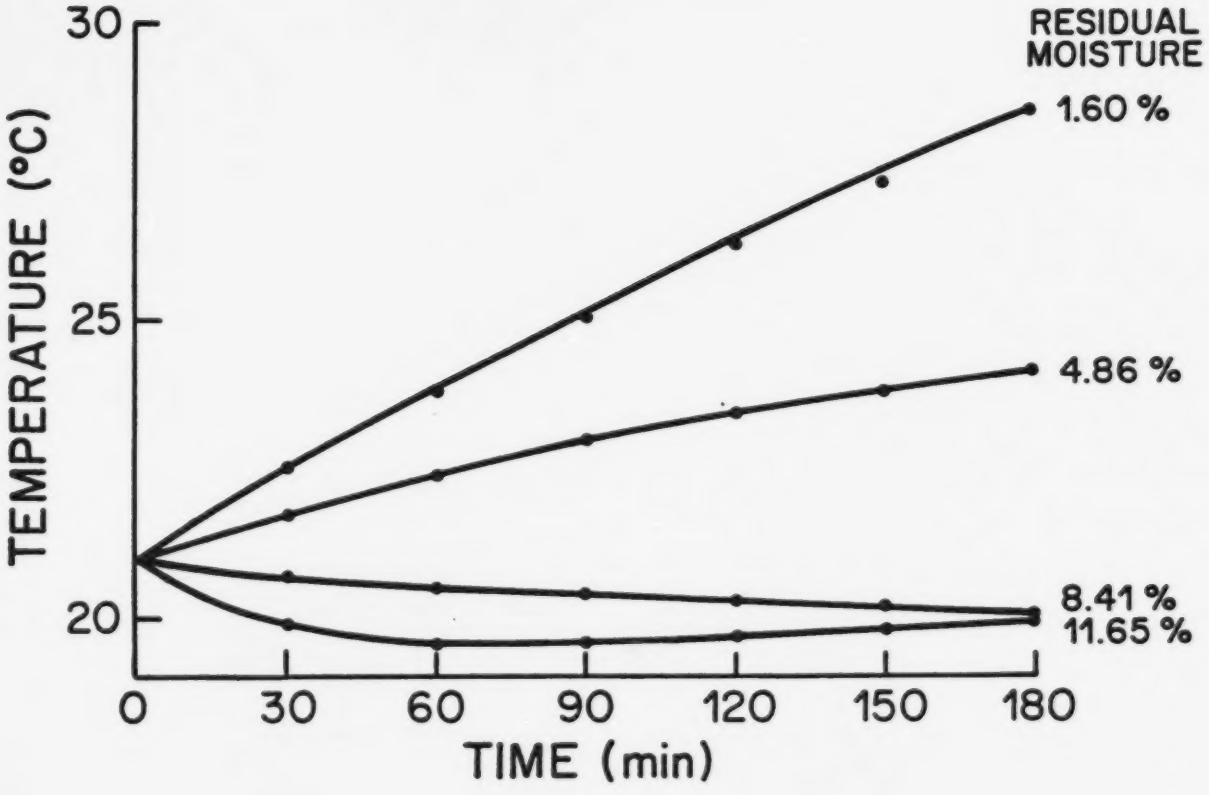


FIGURE 29

TEMPERATURE RESPONSE OF COAL-I TO GAS FLOW
AIR - R.H. 22%

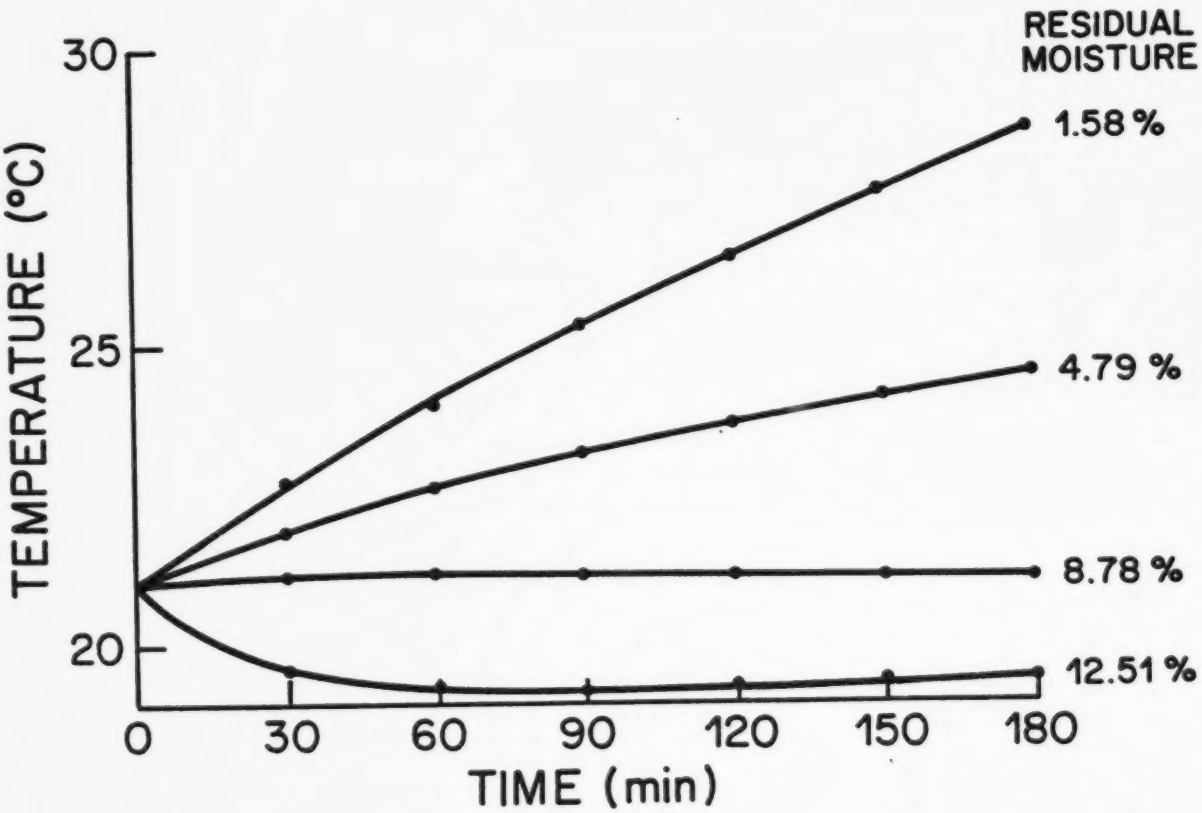


FIGURE 30

TEMPERATURE RESPONSE OF COAL-J TO GAS FLOW
AIR - R.H. 22%

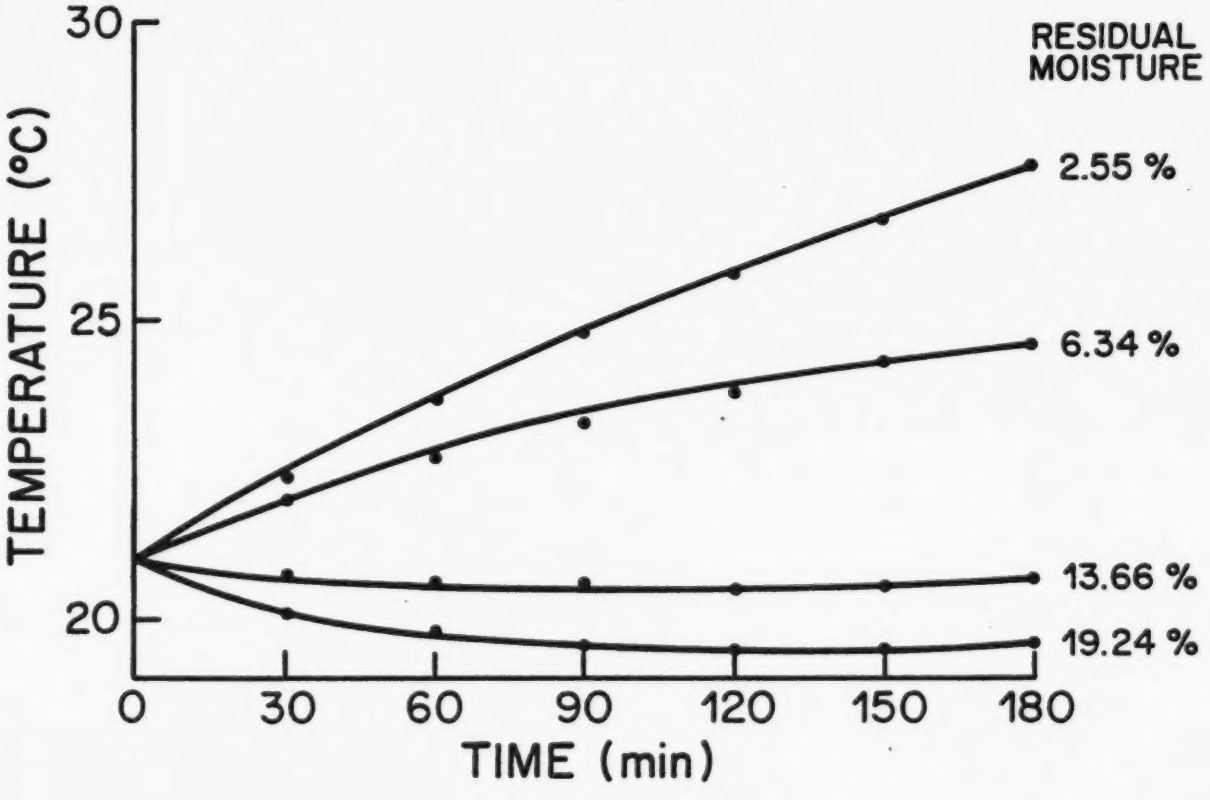


FIGURE 31

TEMPERATURE RESPONSE OF COAL-E TO GAS FLOW
AIR - R.H. 60%

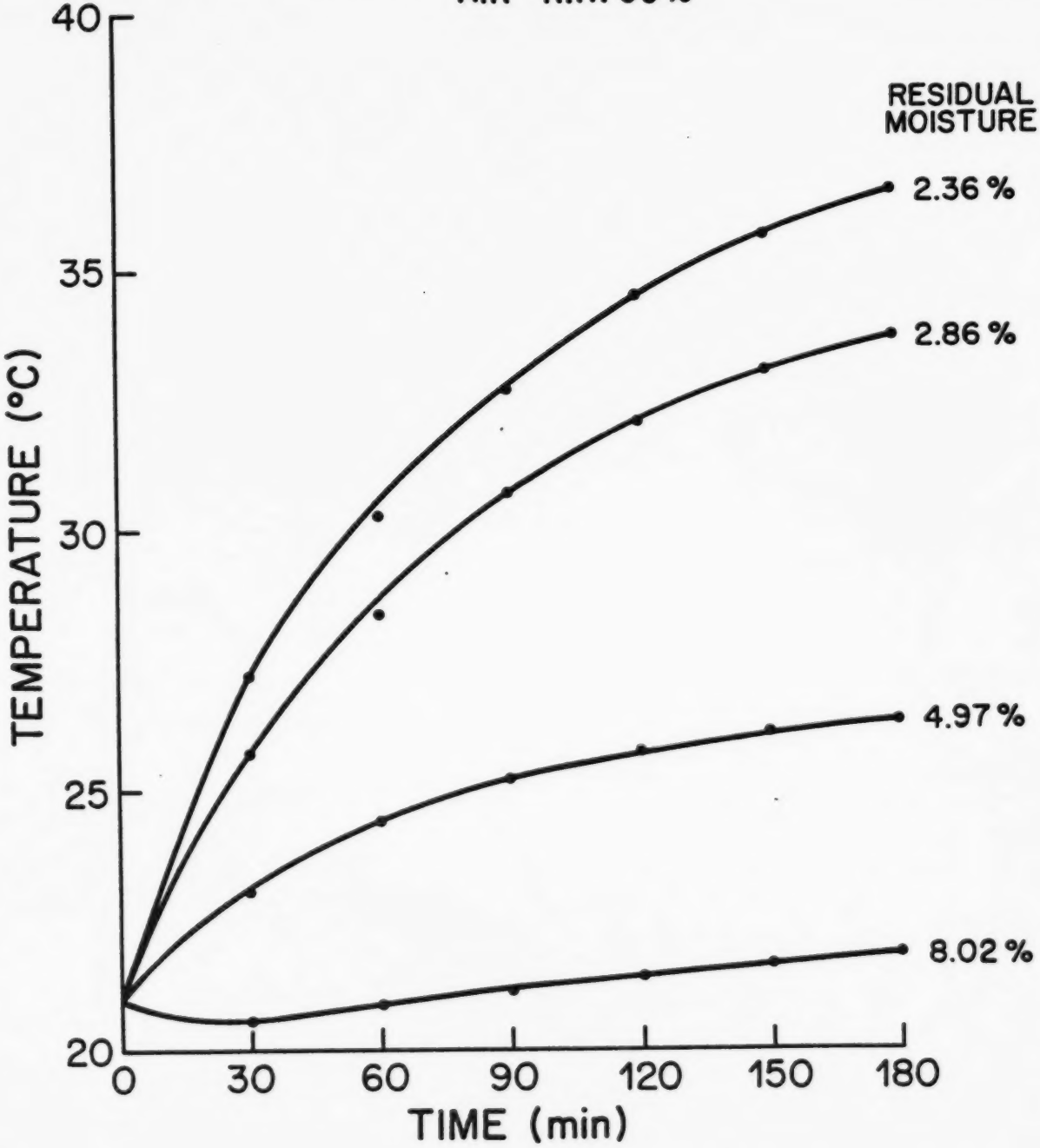


FIGURE 32

TEMPERATURE RESPONSE OF COAL-F TO GAS FLOW
AIR - R.H. 60%

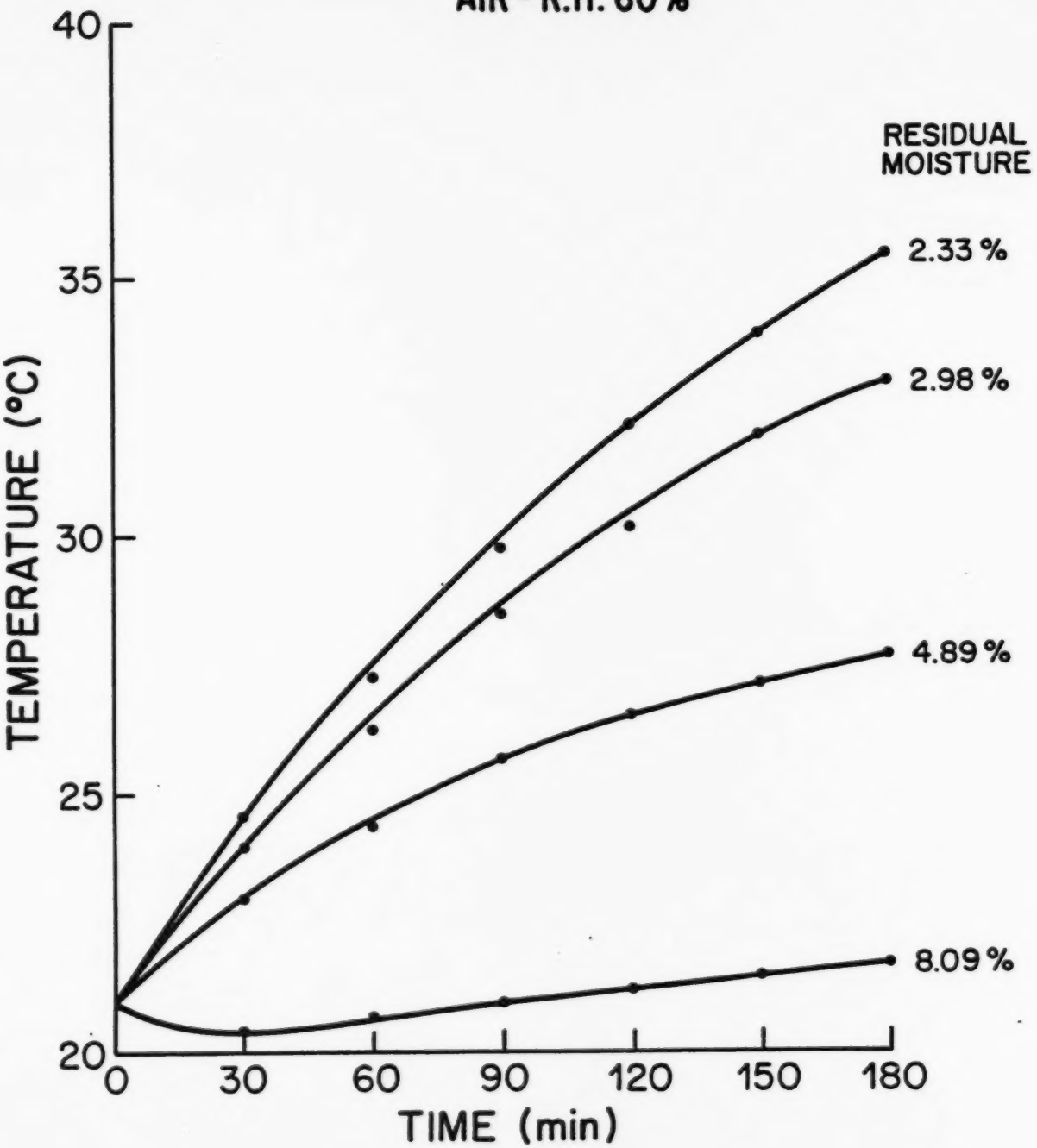


FIGURE 33

TEMPERATURE RESPONSE OF COAL-G TO GAS FLOW
AIR - R.H. 60%

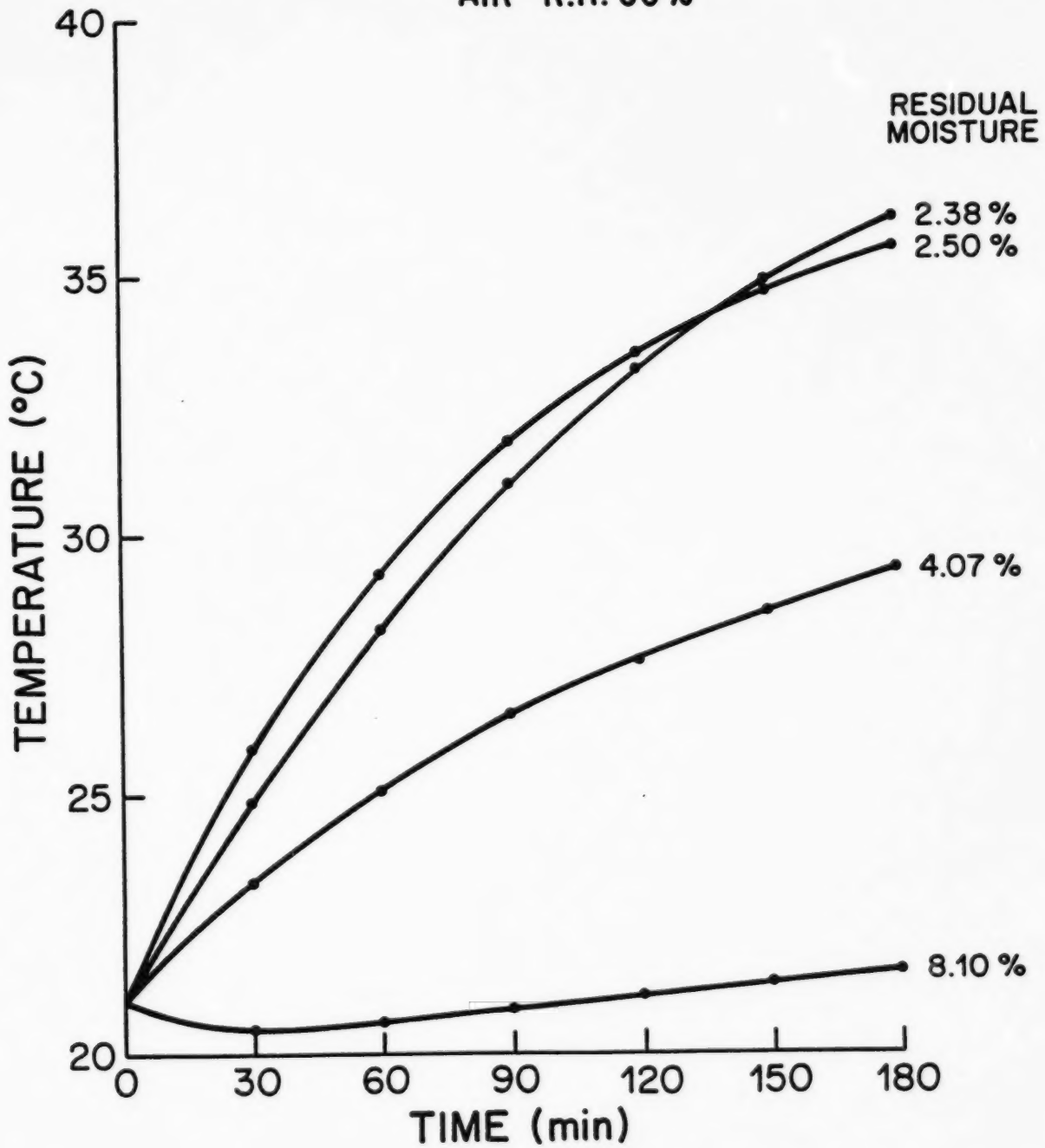


FIGURE 34

TEMPERATURE RESPONSE OF COAL-H TO GAS FLOW
AIR - R.H. 60%

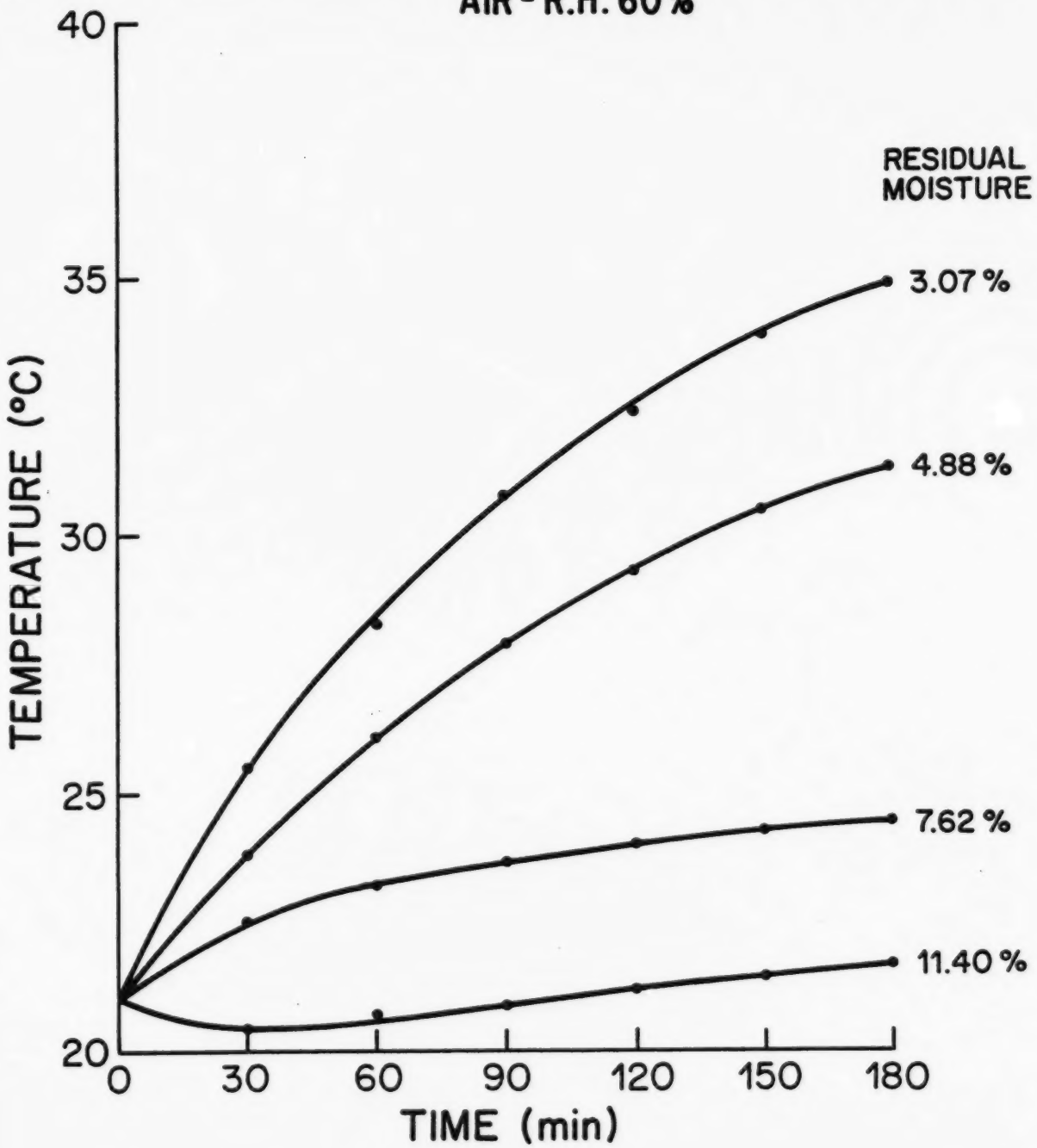


FIGURE 35

TEMPERATURE RESPONSE OF COAL-I TO GAS FLOW
AIR - R.H. 60%

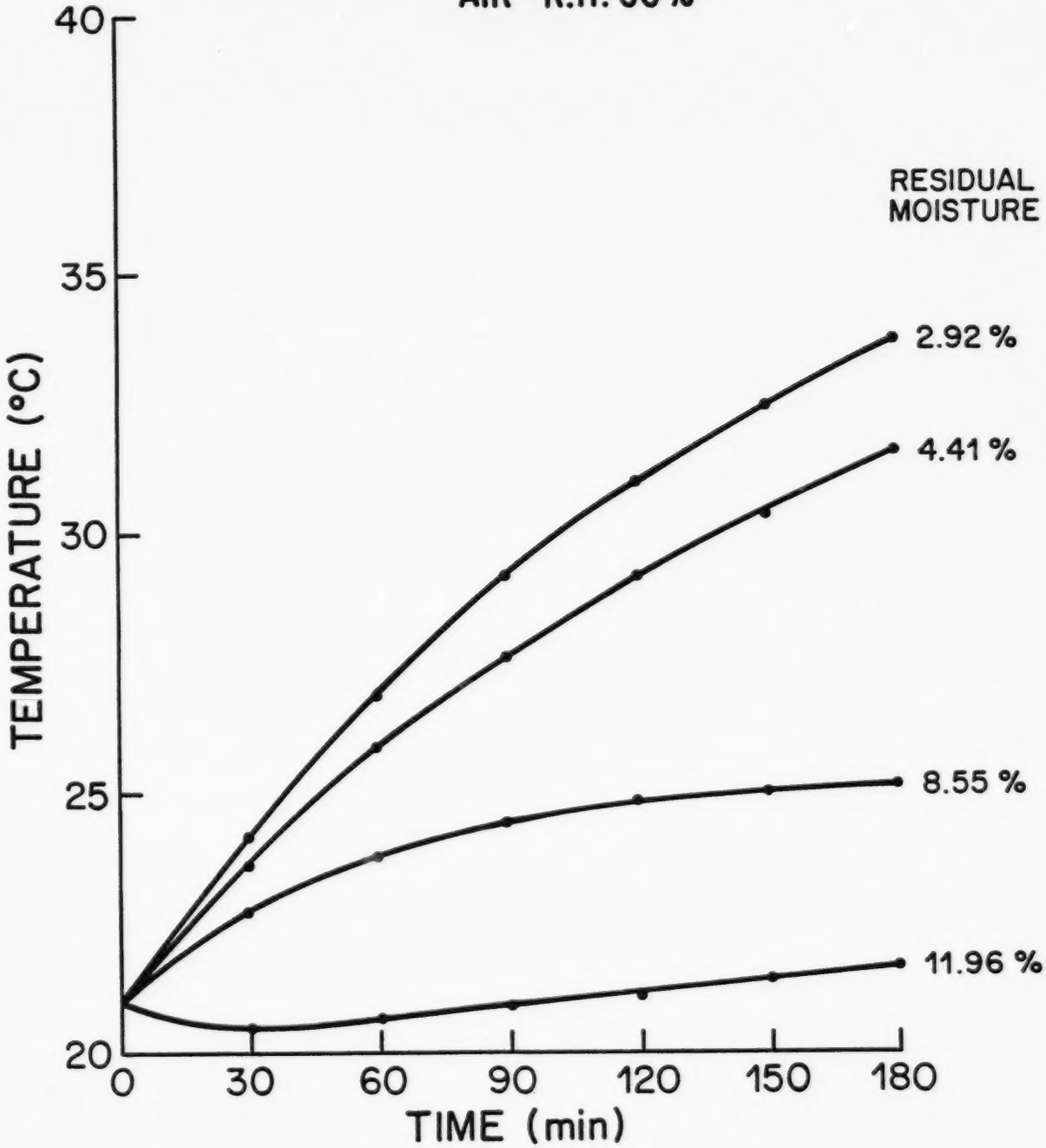


FIGURE 36

TEMPERATURE RESPONSE OF COAL-J TO GAS FLOW
AIR - R.H. 60%

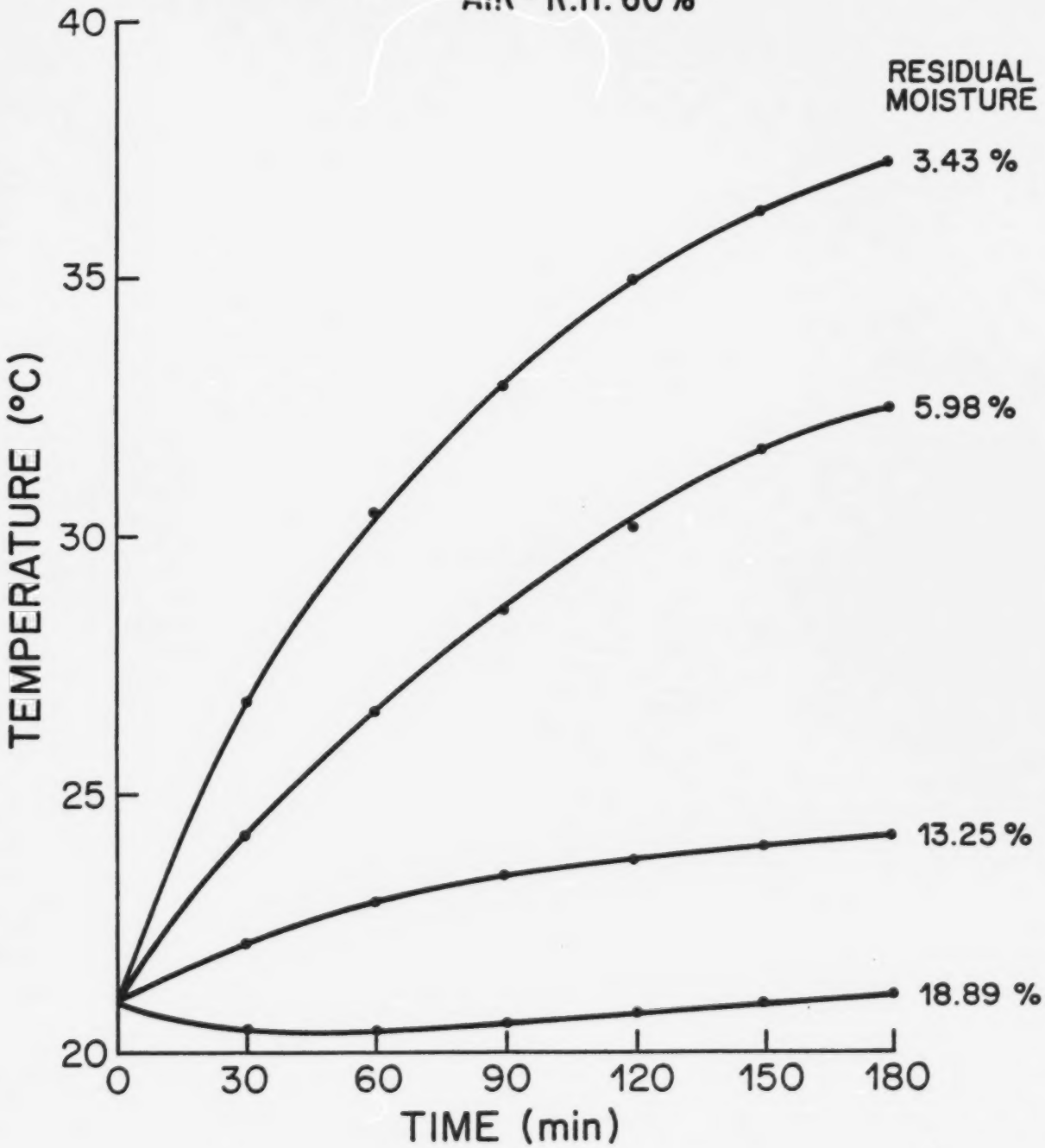


FIGURE 37
TEMPERATURE RESPONSE OF COAL-E TO GAS FLOW
AIR - R.H. 97%

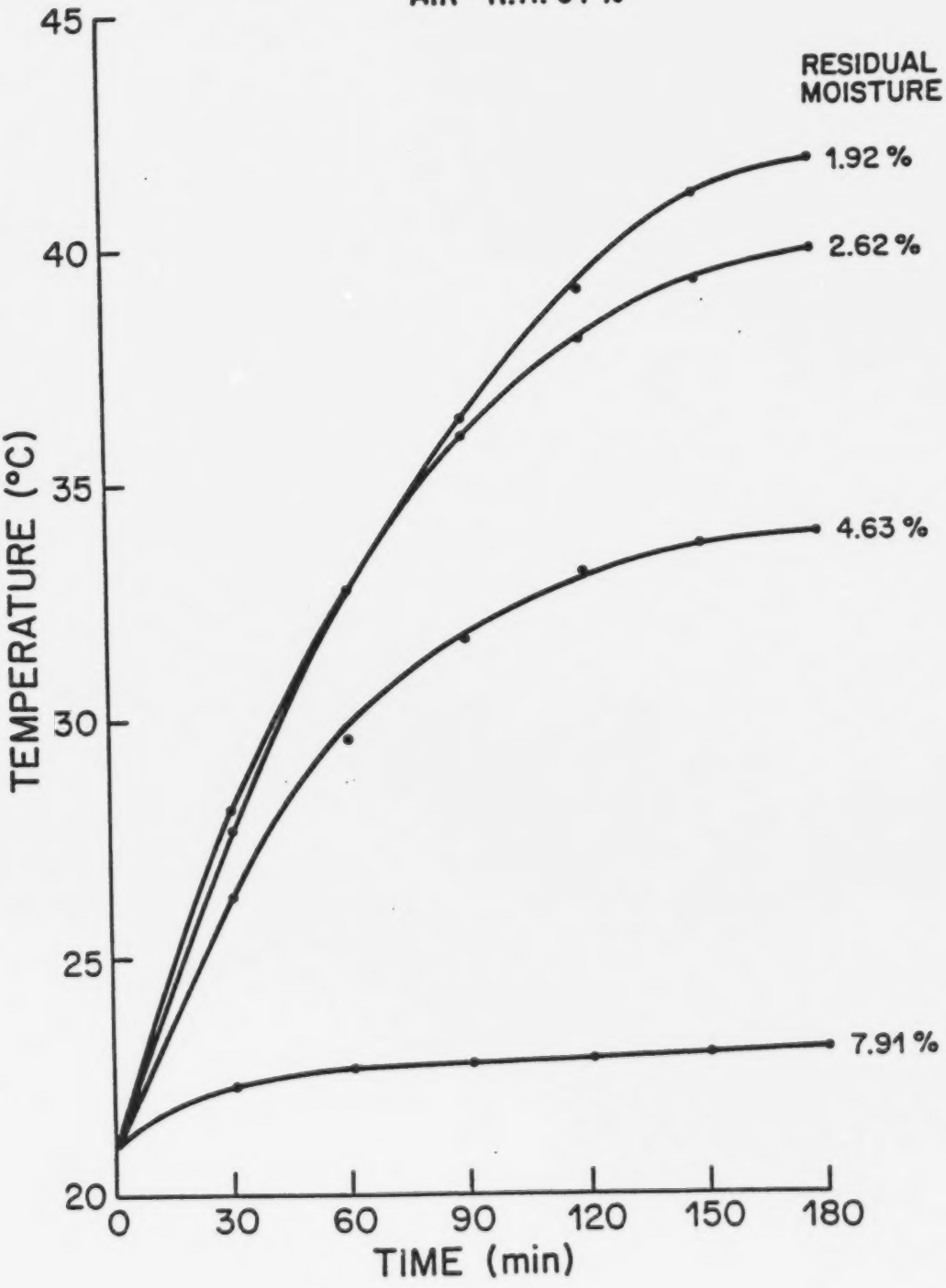


FIGURE 38
TEMPERATURE RESPONSE OF COAL-F TO GAS FLOW
AIR - R.H. 97%

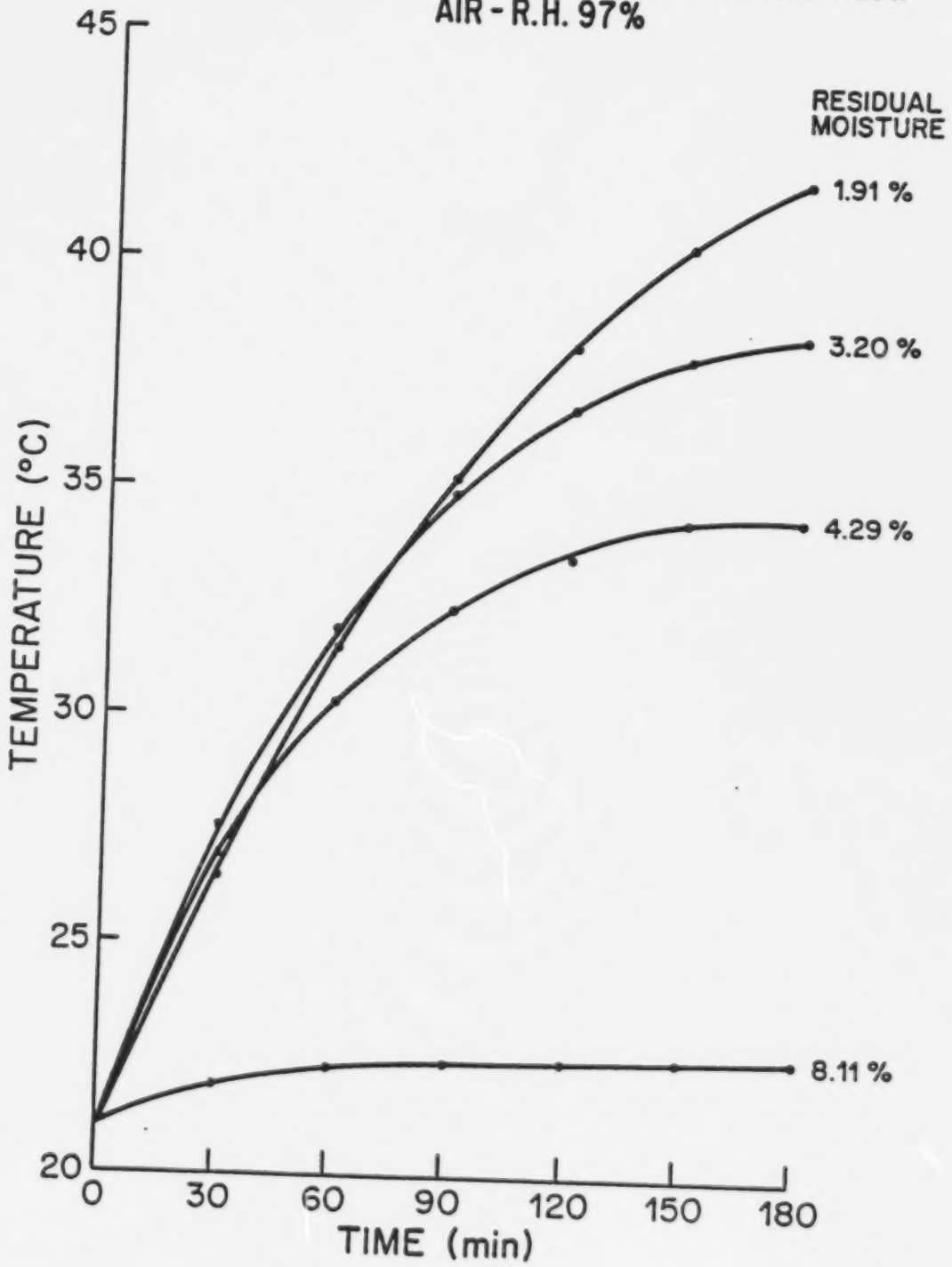


FIGURE 39

TEMPERATURE RESPONSE OF COAL-G TO GAS FLOW
AIR - R.H. 97%

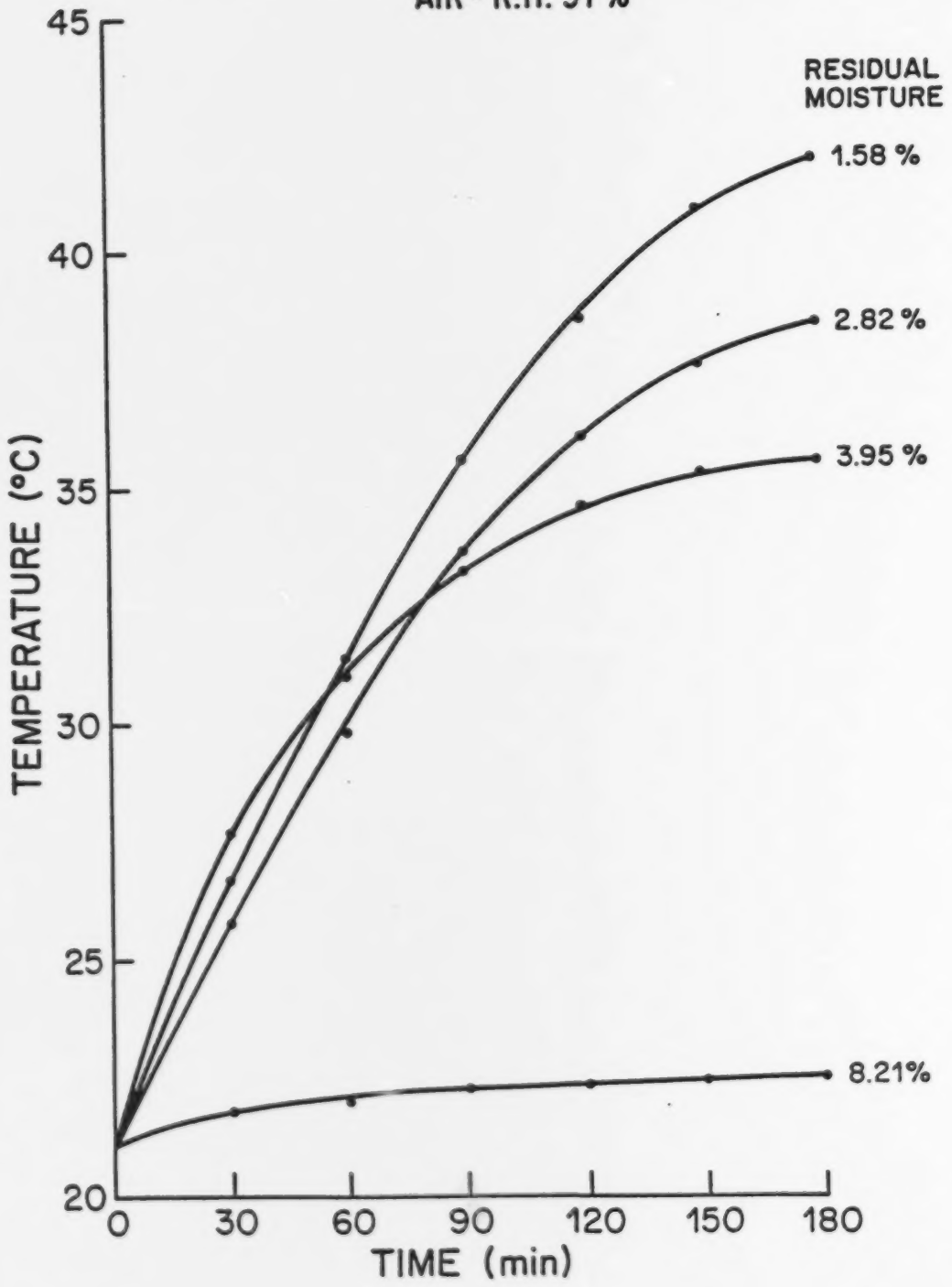


FIGURE 40

TEMPERATURE RESPONSE OF COAL-H TO GAS FLOW
AIR - R.H. 97%

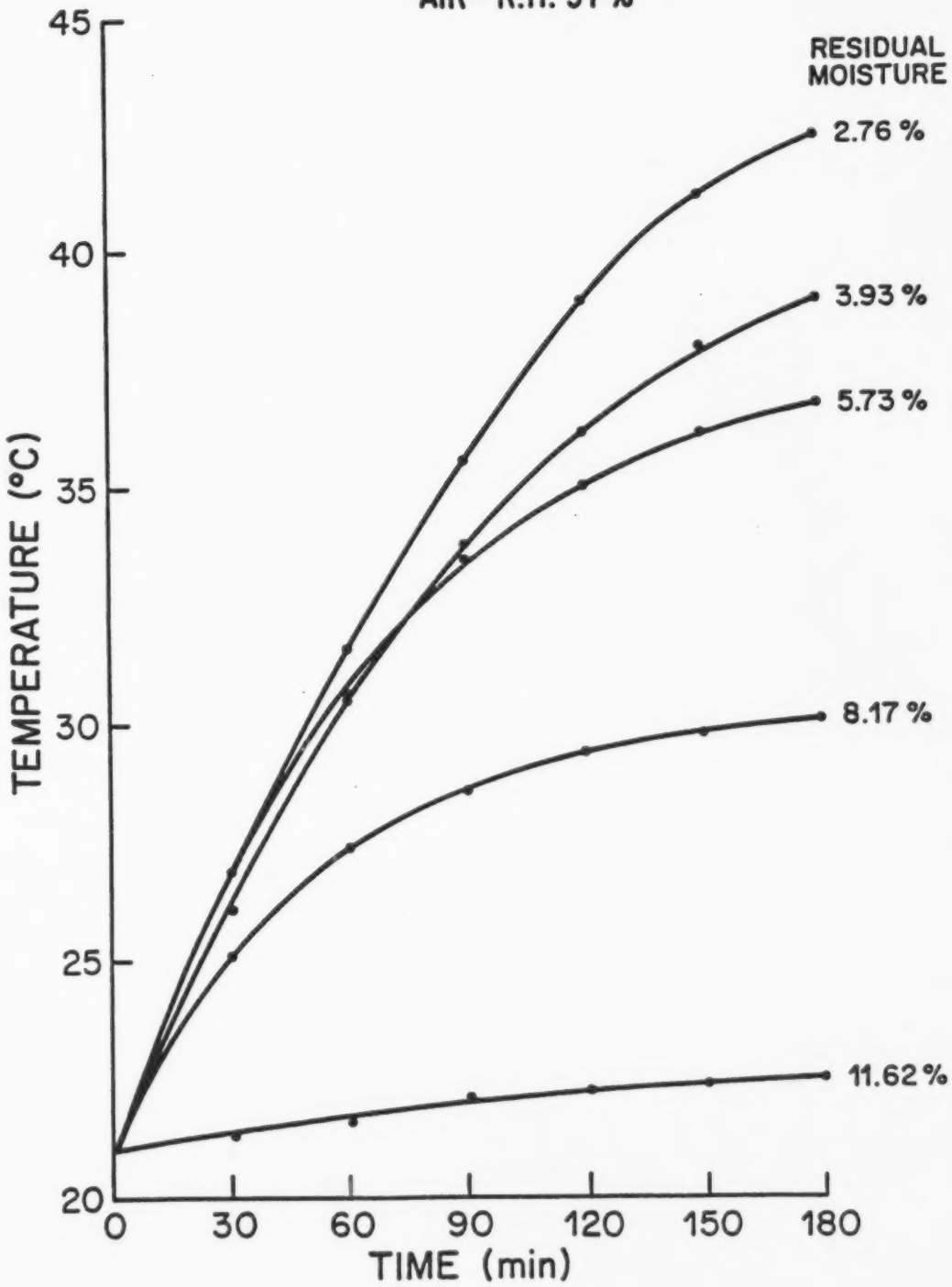


FIGURE 41

TEMPERATURE RESPONSE OF COAL-I TO GAS FLOW
AIR - R.H. 97%

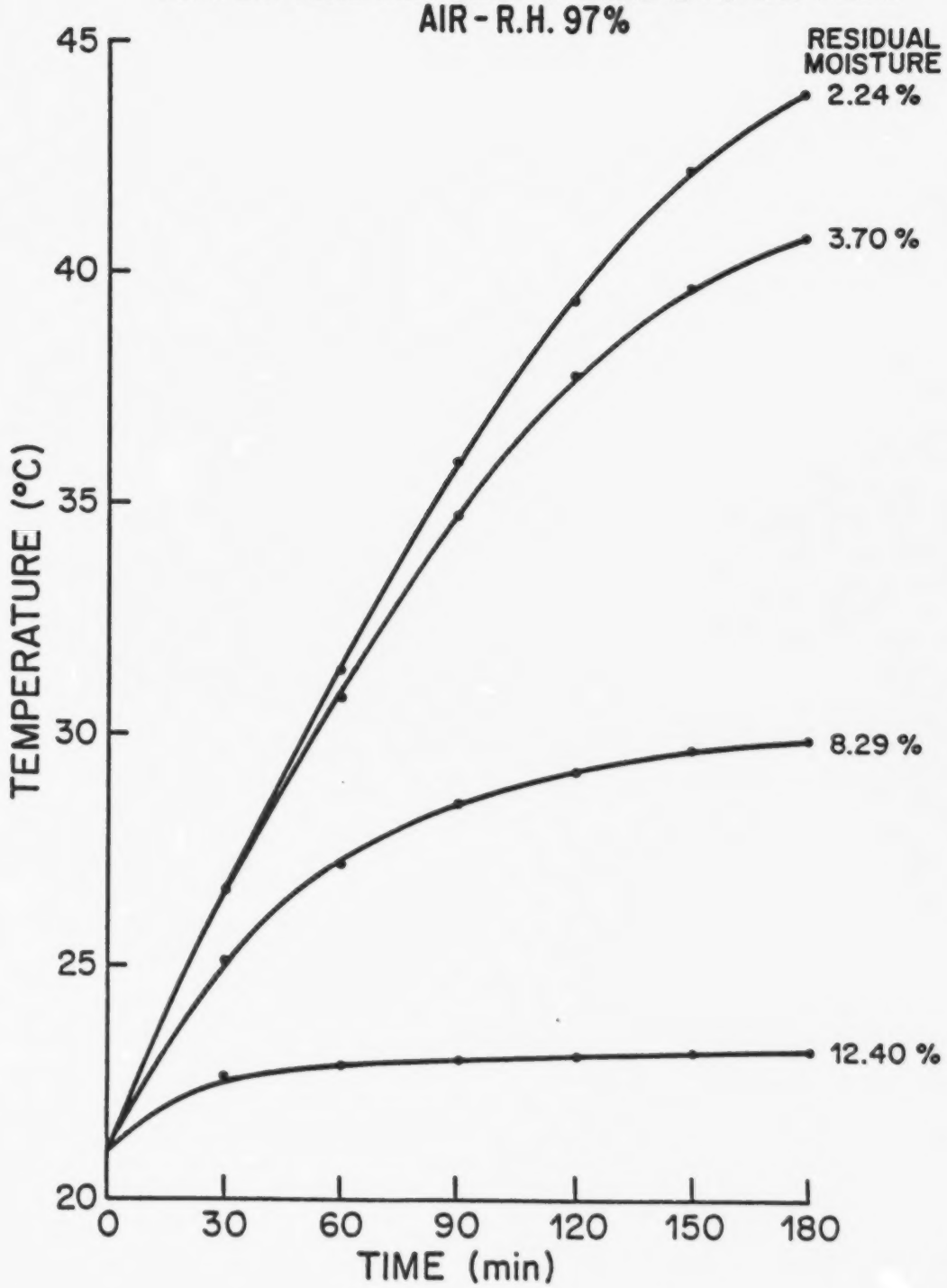


FIGURE 42

TEMPERATURE RESPONSE OF COAL-J TO GAS FLOW
AIR - R.H. 97%

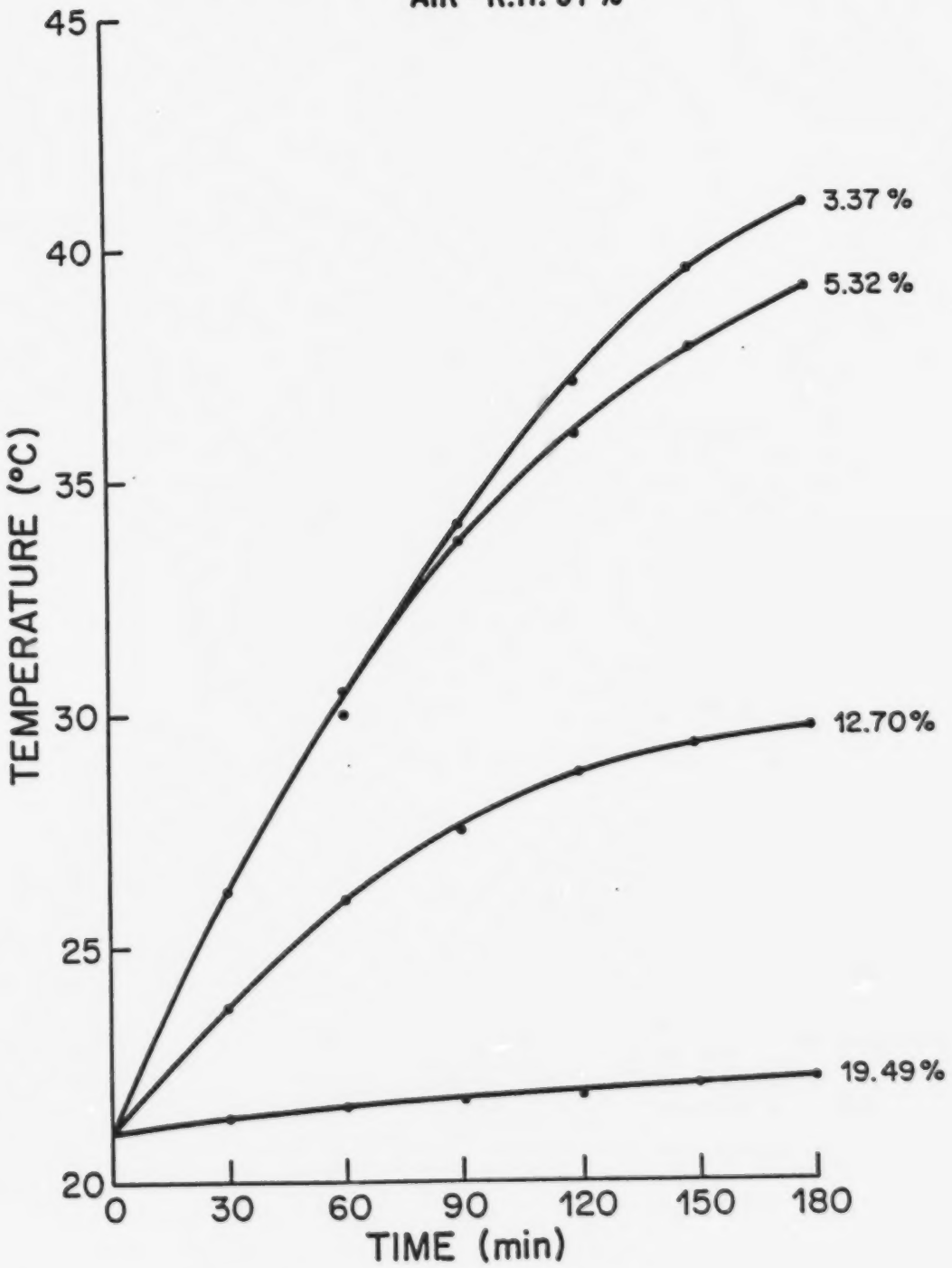


FIGURE 43

TEMPERATURE RESPONSE OF COAL SAMPLES TO GAS FLOW AIR - R.H. 60%

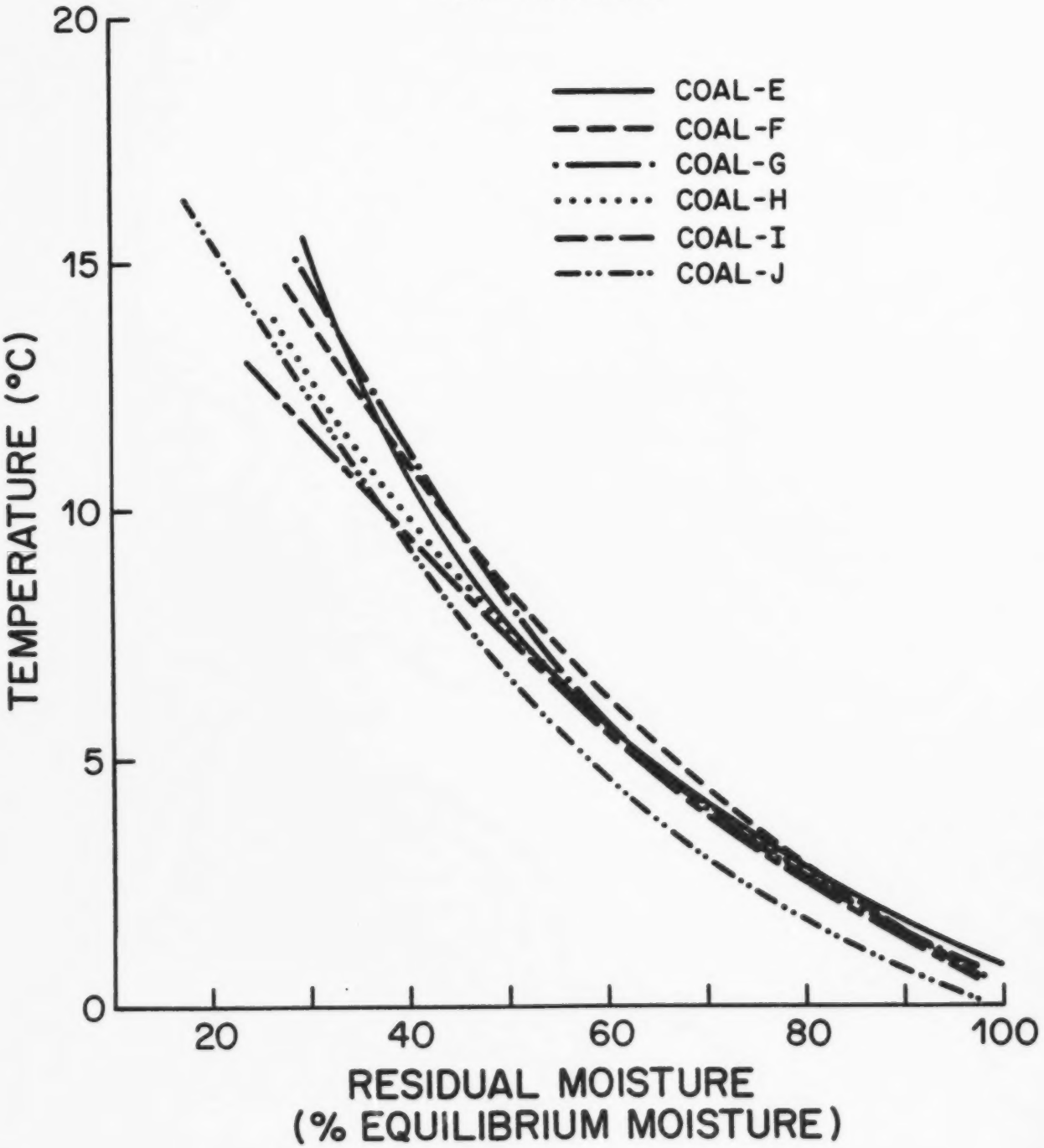


FIGURE 44

TEMPERATURE RESPONSE OF COAL-I
TO GAS FLOW OF VARYING RELATIVE HUMIDITIES

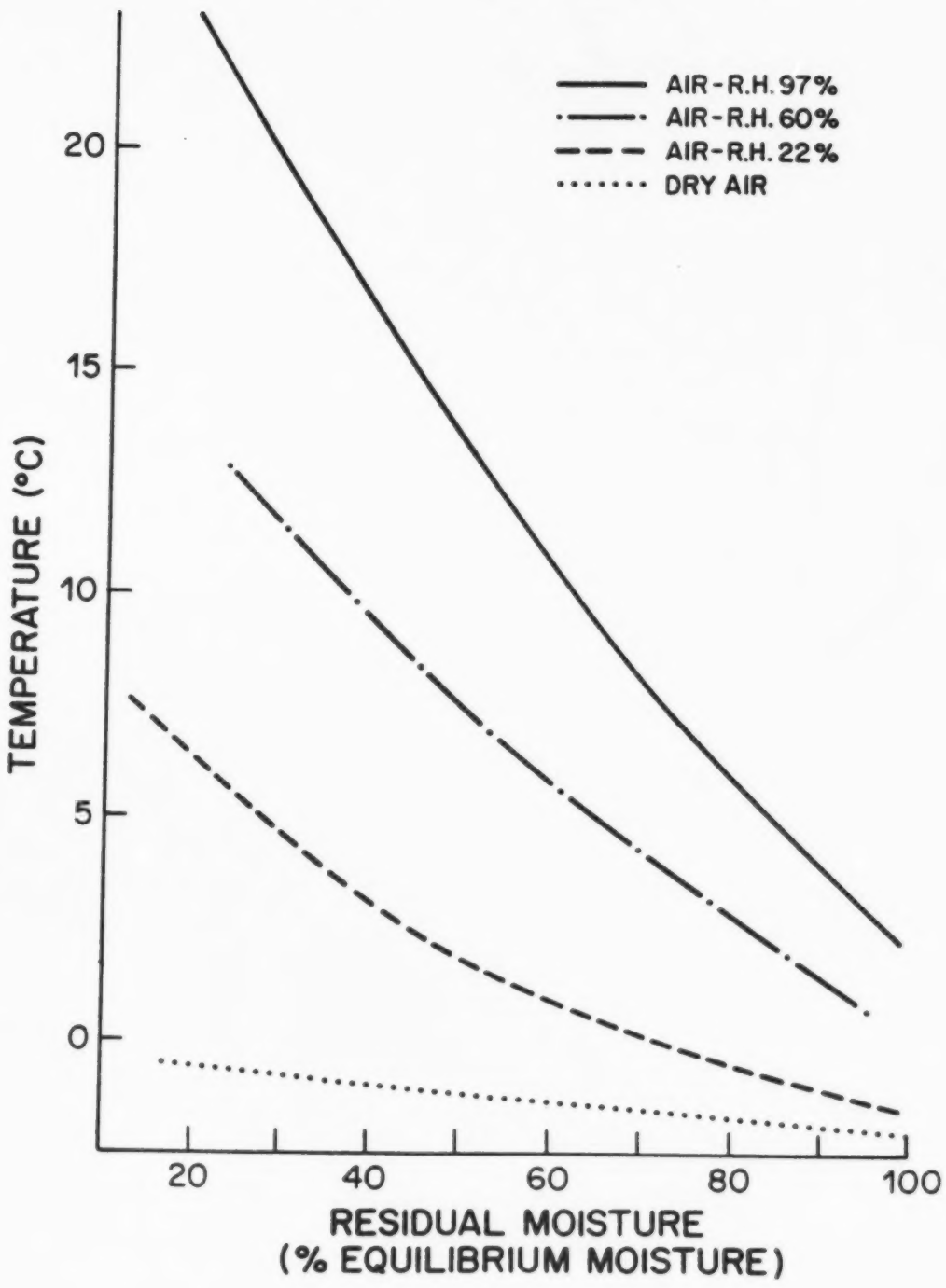


FIGURE 45
DRIFT ANALYSES OF COAL SAMPLES

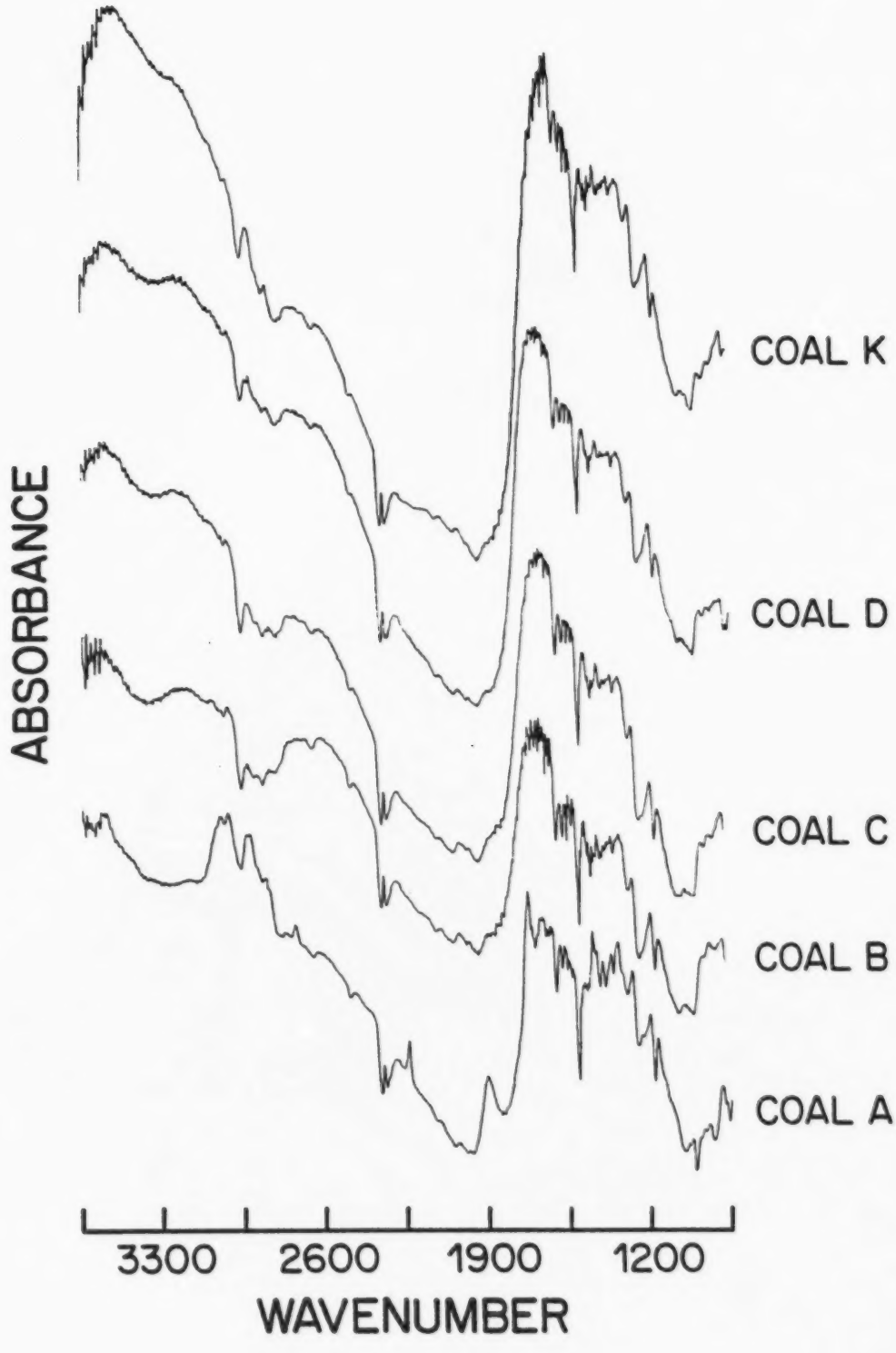


FIGURE 46

DRIFT ANALYSES OF COAL SAMPLES
WINDOW 3060-2860 cm^{-1}

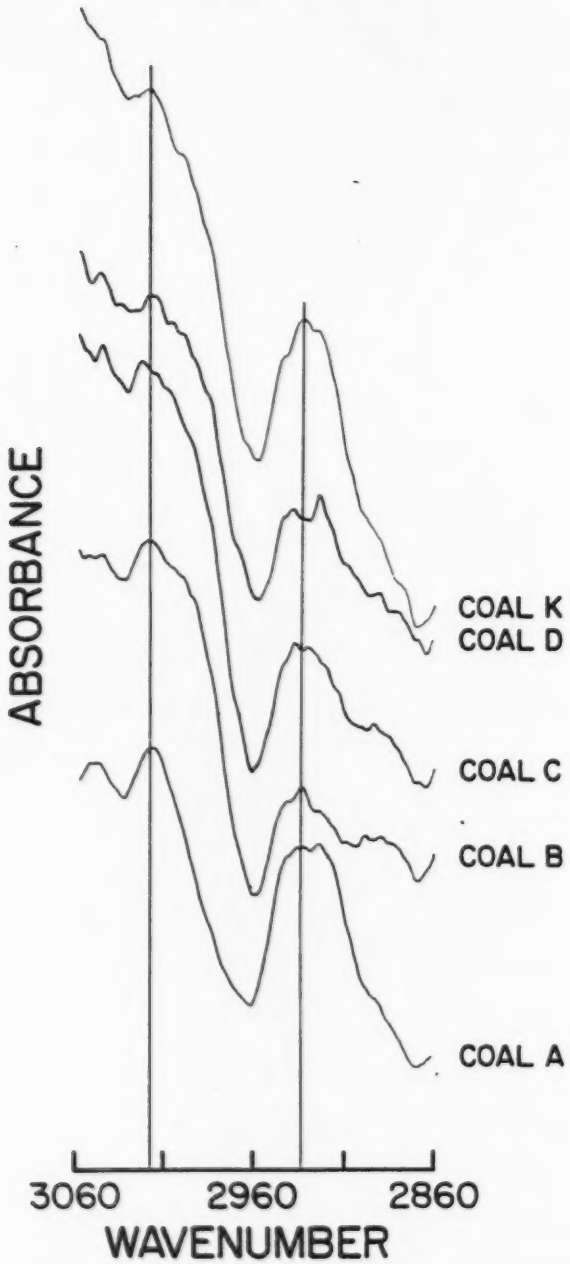


FIGURE 47
DRIFT ANALYSES OF COAL SAMPLES
WINDOW 1750-1550 cm^{-1}

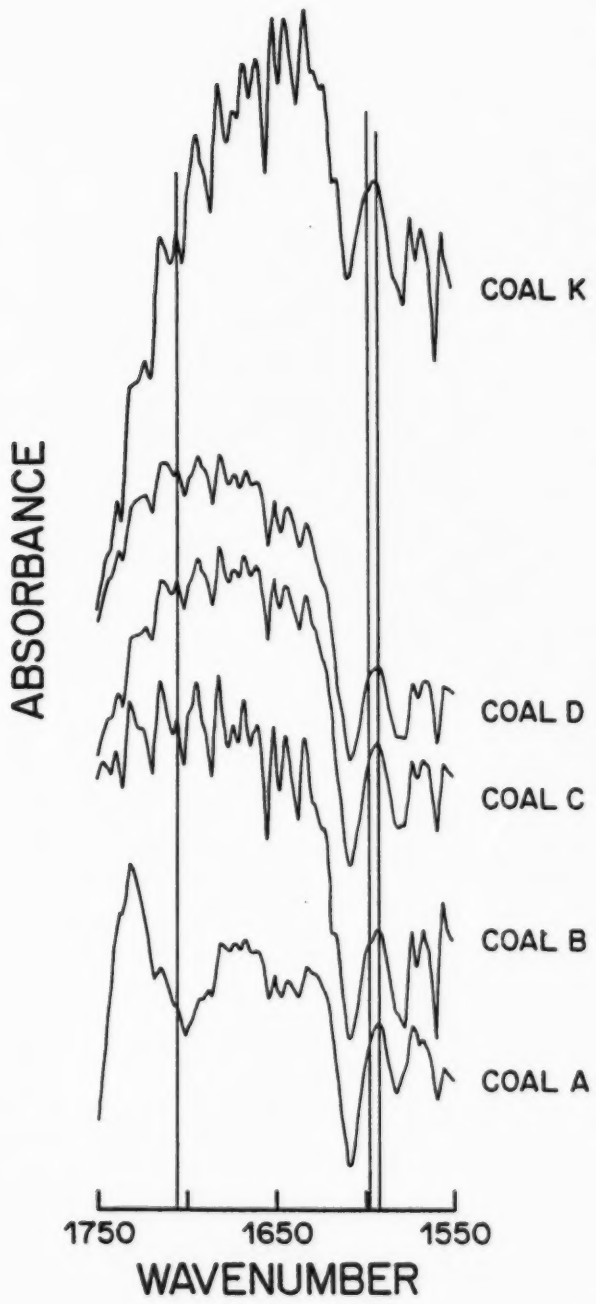


FIGURE 48

DRIFT ANALYSES OF COAL SAMPLES
WINDOW 1510-1410 cm^{-1}

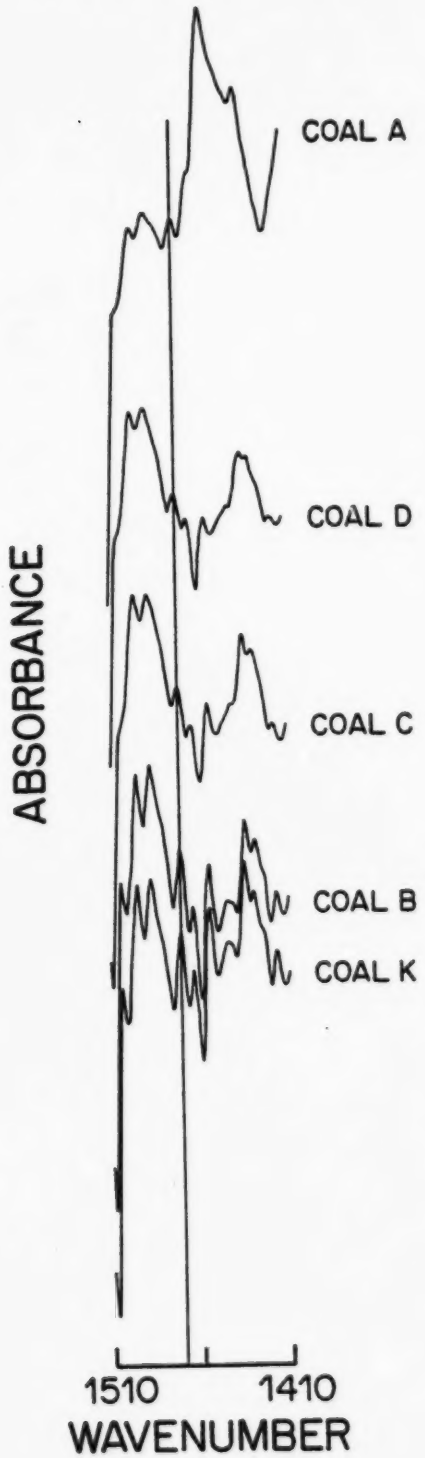
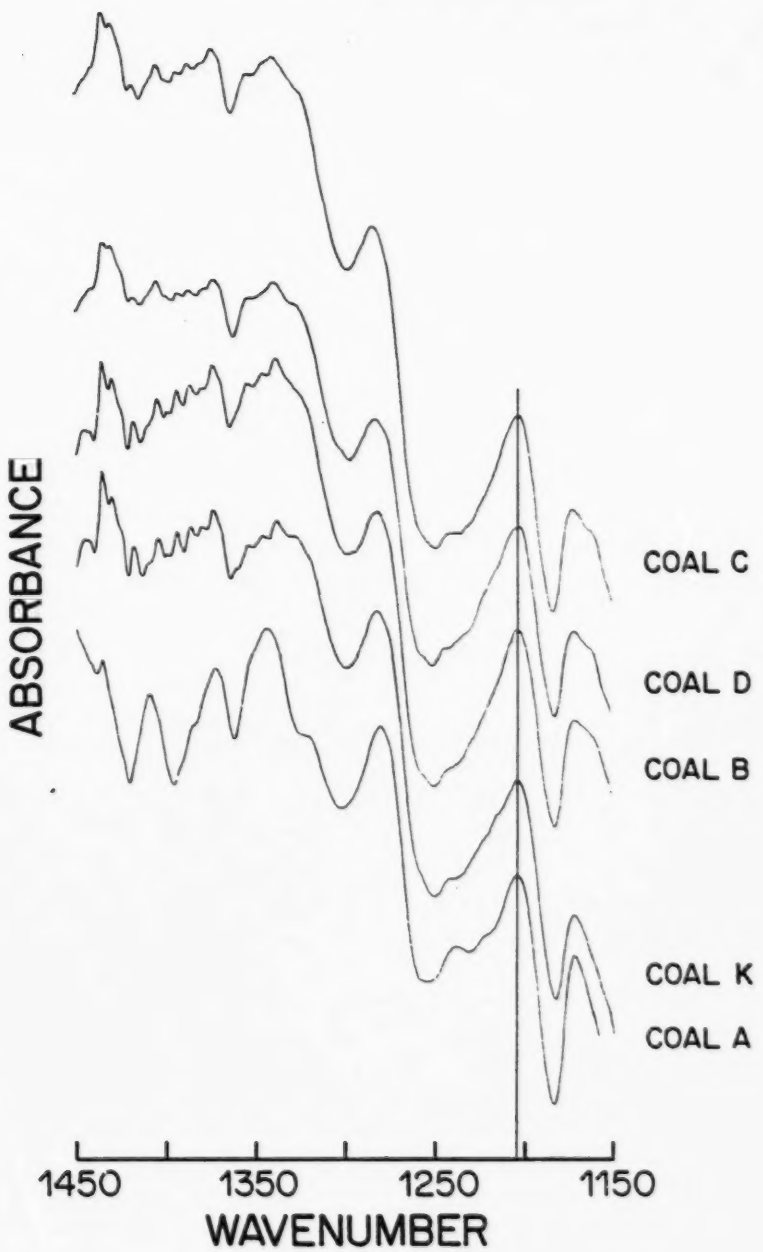


FIGURE 49
DRIFT ANALYSES OF COAL SAMPLES
WINDOW 1450-1150 cm^{-1}



Legend for Figures 50 to 55

DRIFT analysis of Coal-B (Sequential gas flow experiments)

I	Coal-B equilibrated at R.H. 97%
II	Equilibrated coal (I) dried over P_2O_5/vacuum
III	Dried coal (II) treated with moist nitrogen (R.H. 97%) flow.
IV	Coal (III) redried over P_2O_5/vacuum and treated again with moist nitrogen (R.H. 97%) flow.
V	Coal (IV) redried over P_2O_5/vacuum and treated with moist air (R.H. 97%) flow.

FIGURE 50

DRIFT ANALYSIS OF COAL-B
SEQUENTIAL GAS FLOW EXPERIMENTS

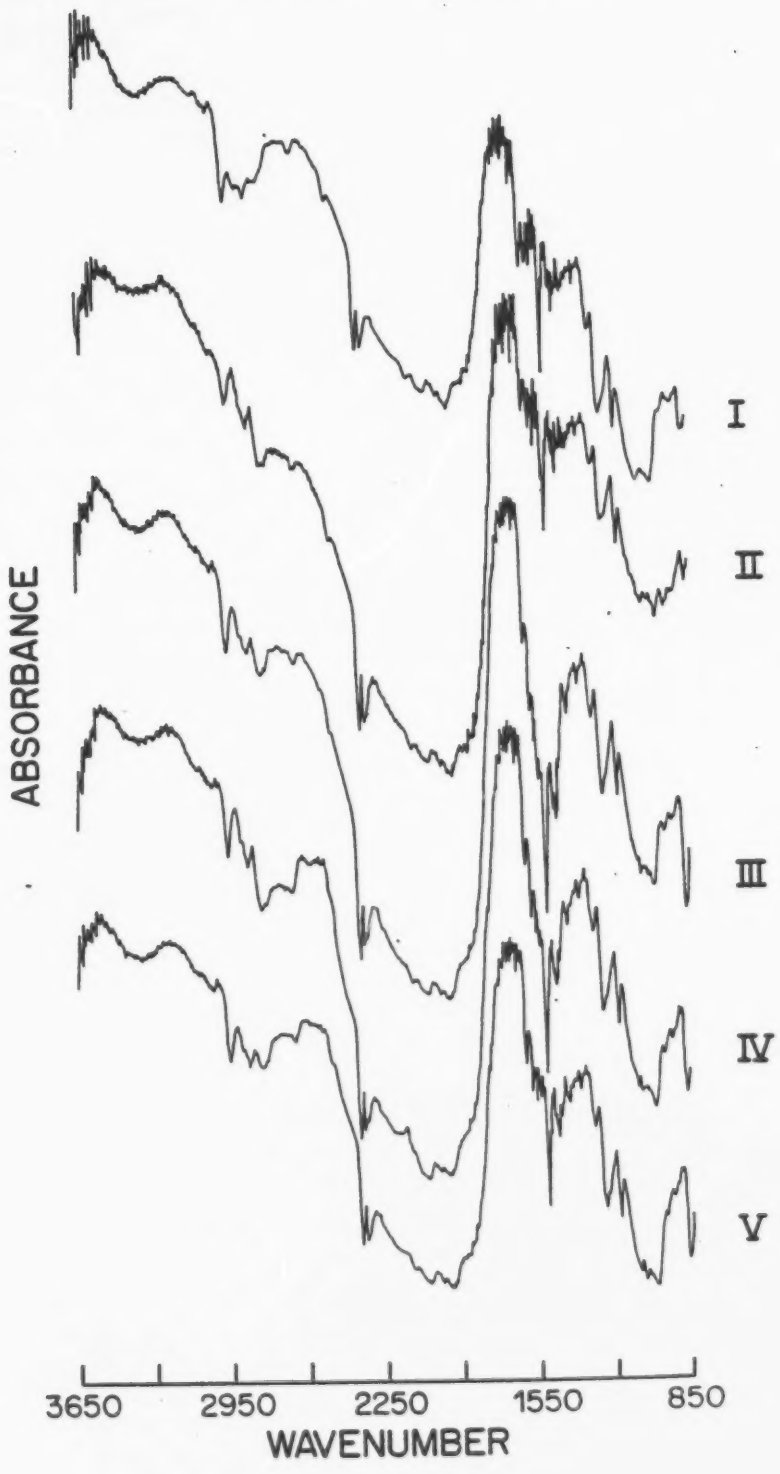


FIGURE 51

DRIFT ANALYSIS OF COAL-B
SEQUENTIAL GAS FLOW EXPERIMENTS
WINDOW 3060-2860 cm^{-1}

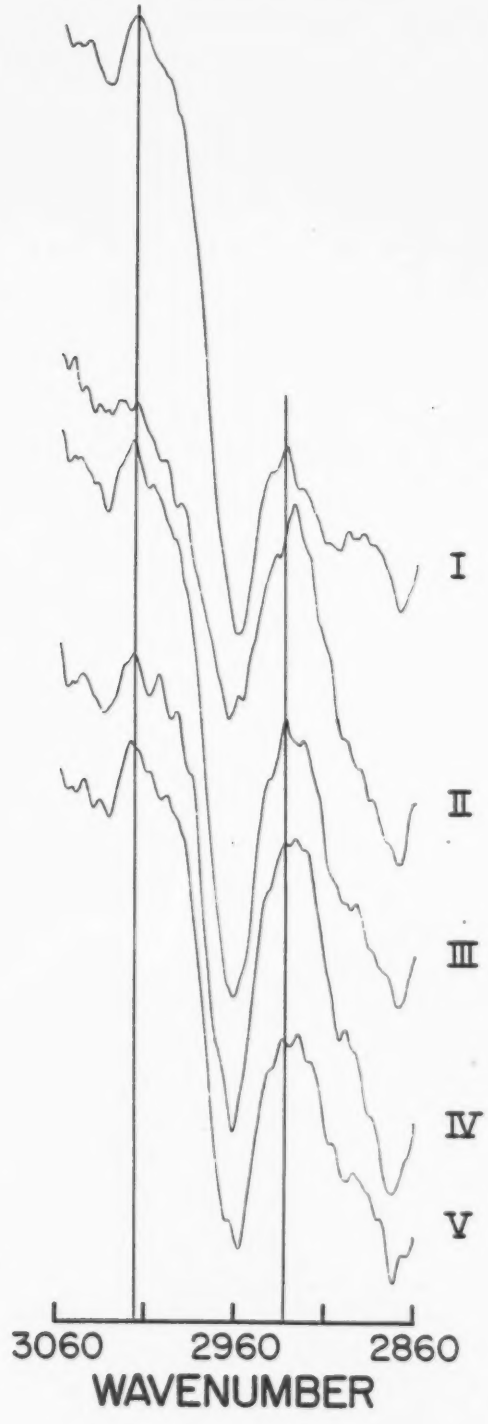


FIGURE 52

DRIFT ANALYSIS OF COAL-B
SEQUENTIAL GAS FLOW EXPERIMENTS
WINDOW 1750 - 1550 cm^{-1}

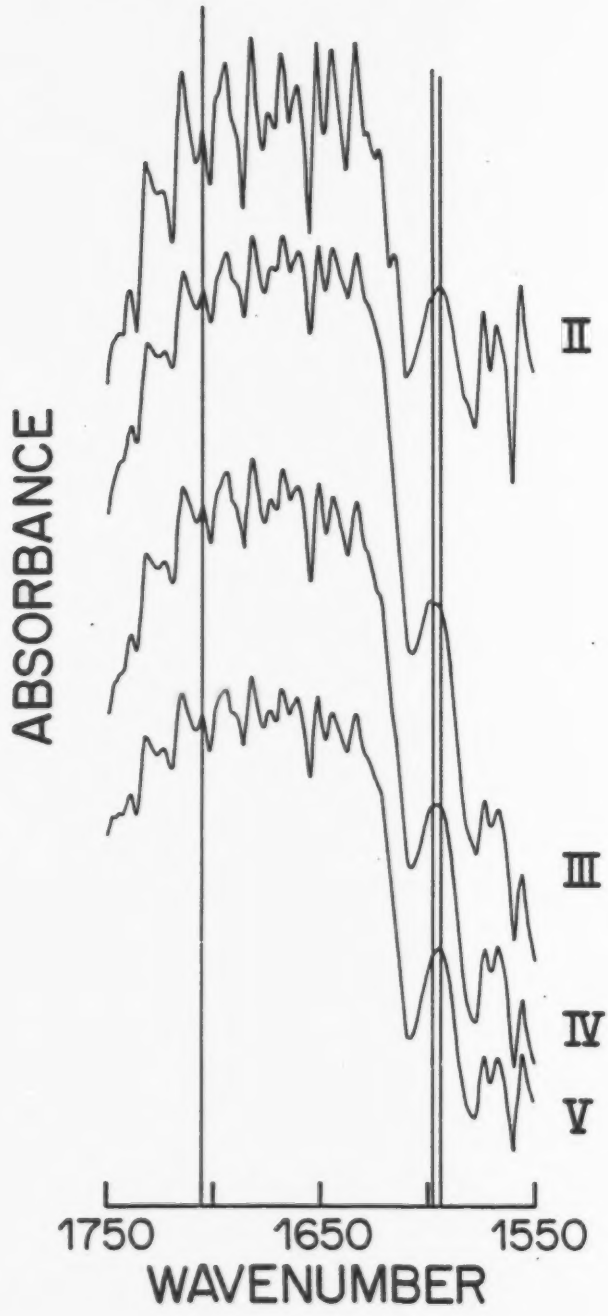


FIGURE 53

DRIFT ANALYSIS OF COAL-B
SEQUENTIAL GAS FLOW EXPERIMENTS
WINDOW 1510 - 1410 cm^{-1}

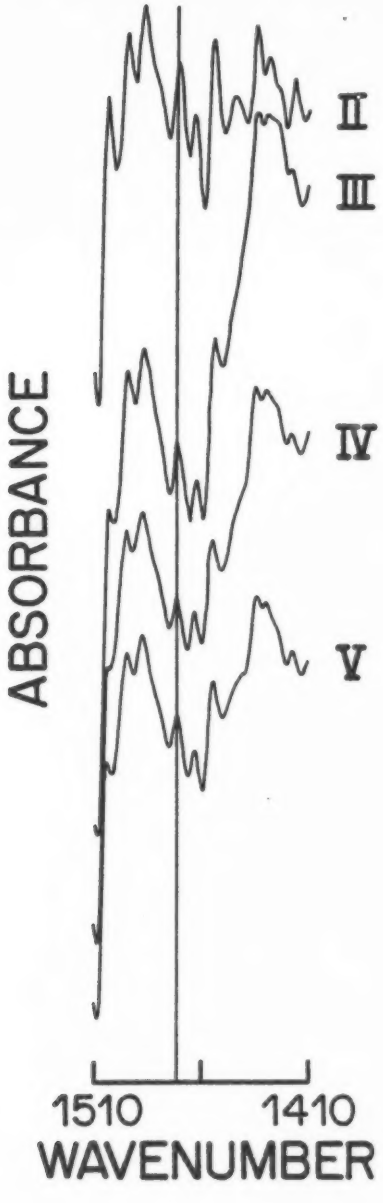


FIGURE 54

DRIFT ANALYSIS OF COAL-B
SEQUENTIAL GAS FLOW EXPERIMENTS
WINDOW 1450-1150 cm^{-1}

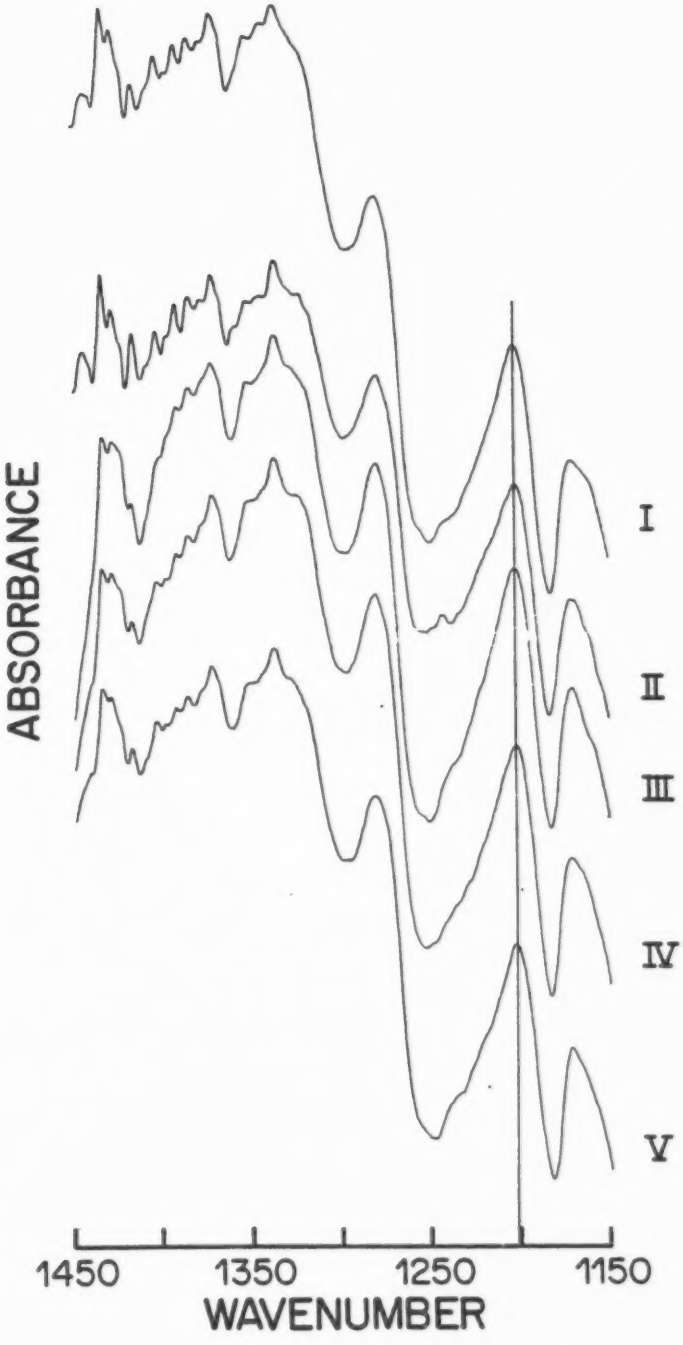
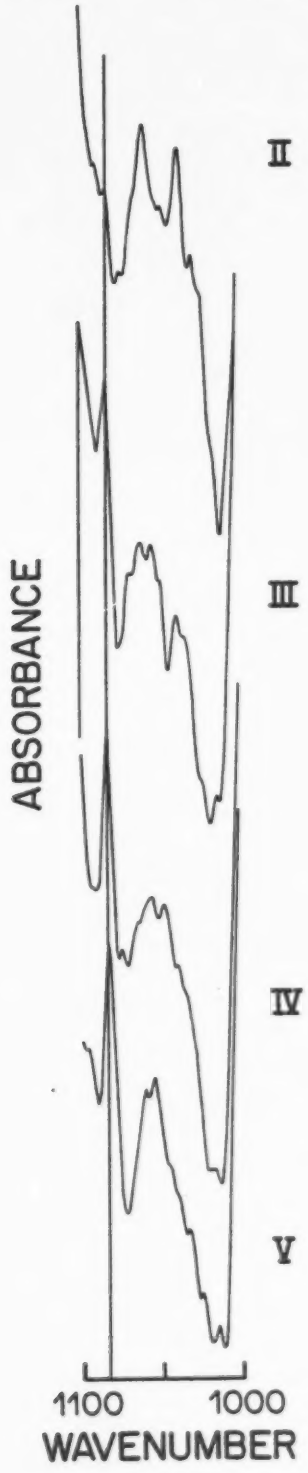


FIGURE 55

DRIFT ANALYSIS OF COAL-B
SEQUENTIAL GAS FLOW EXPERIMENTS
WINDOW 1100-1000 cm^{-1}



Legend for Figures 56 to 61

DRIFT analysis of Coal-B (Moisture saturated air flow experiment)

I Coal-B equilibrated at R.H. 97%

II Equilibrated coal (I) dried over P_2O_5/vacuum

III Dried coal (II) treated with moist air (R.H. 97%) flow.

IV Coal (III) redried over P_2O_5/vacuum and treated again with moist air (R.H. 97%) flow.

FIGURE 56

DRIFT ANALYSIS OF COAL-B
MOISTURE SATURATED AIR FLOW EXPERIMENTS

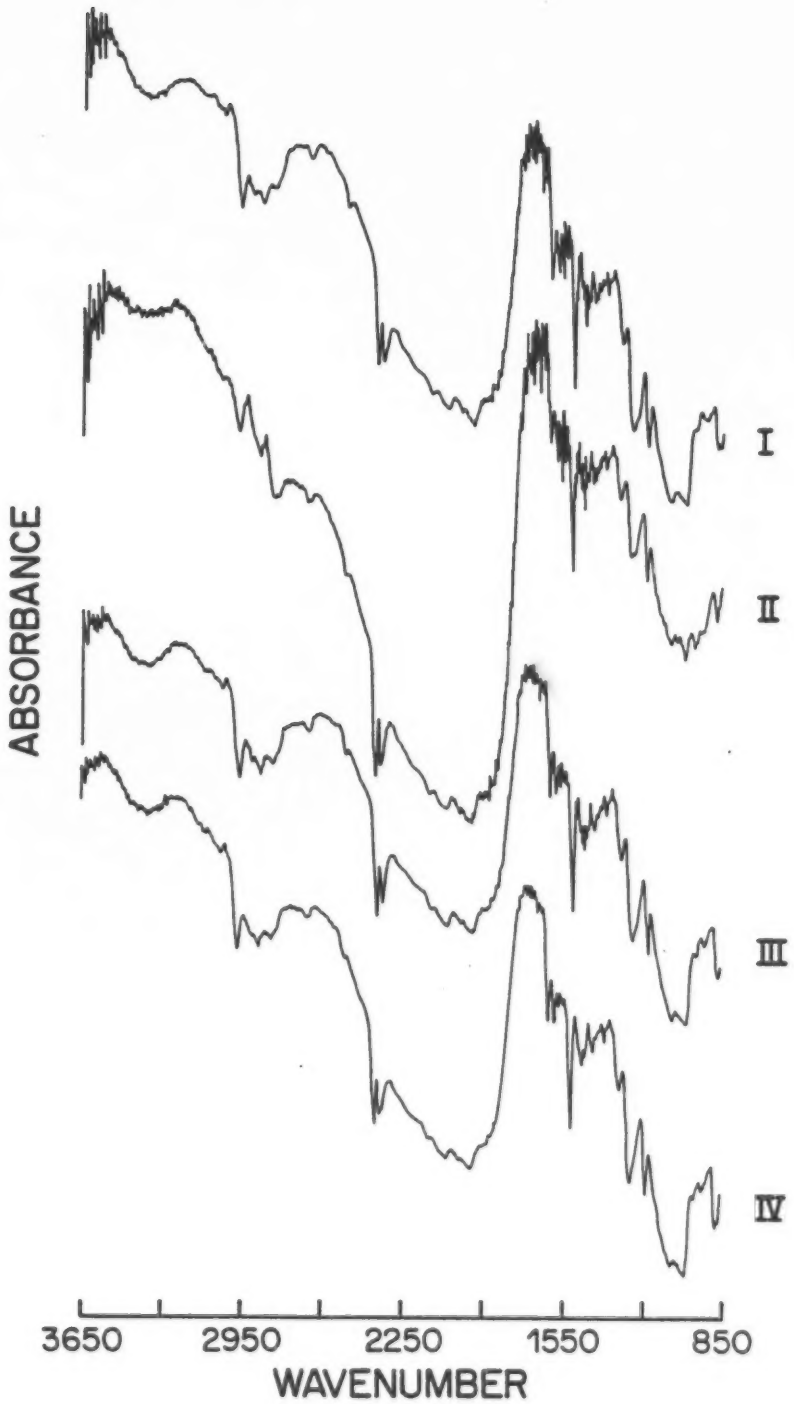


FIGURE 57

DRIFT ANALYSIS OF COAL-B
MOISTURE SATURATED AIR FLOW
EXPERIMENTS - WINDOW 3060 - 2860 cm^{-1}

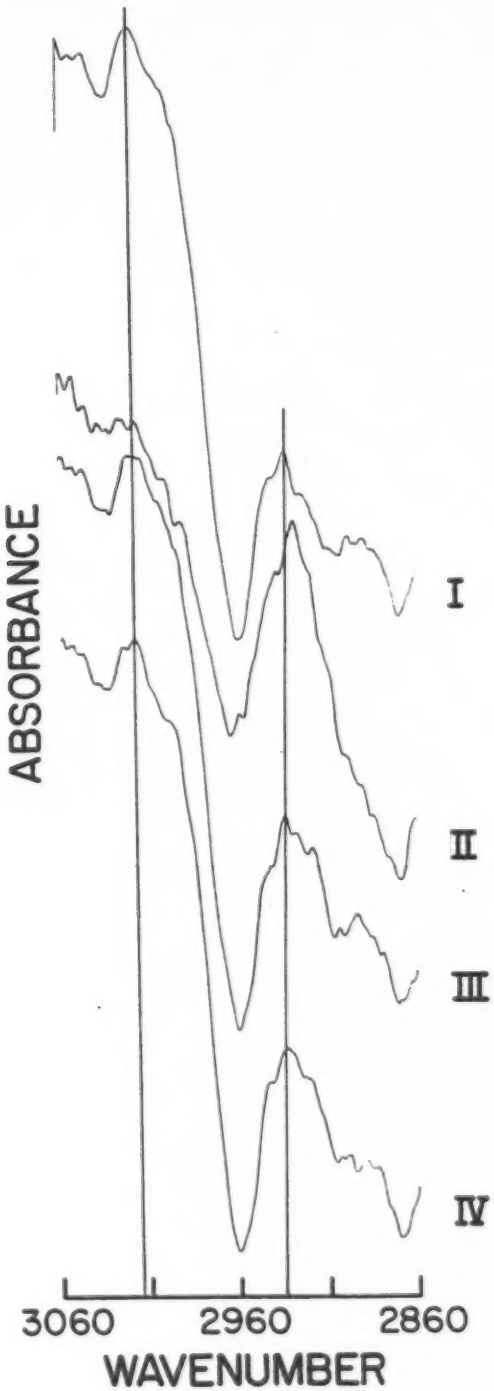


FIGURE 58

DRIFT ANALYSIS OF COAL-B
MOISTURE SATURATED AIR FLOW
EXPERIMENTS - WINDOW 1750-1550 cm^{-1}

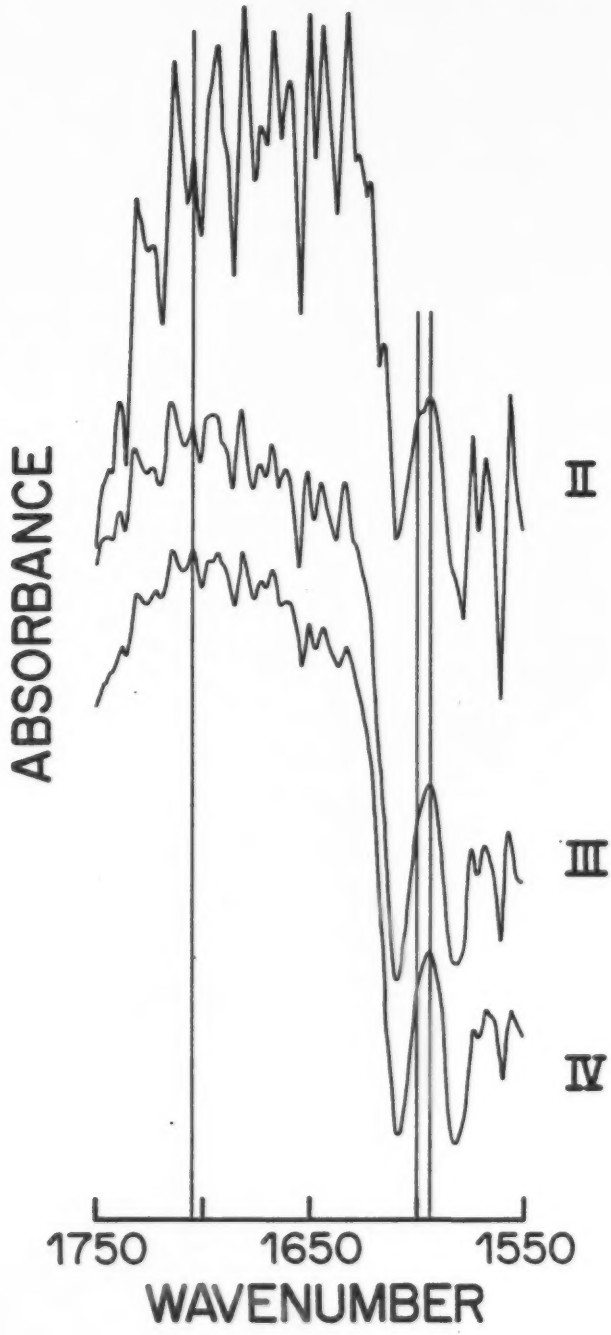


FIGURE 59

DRIFT ANALYSIS OF COAL-B
MOISTURE SATURATED AIR FLOW
EXPERIMENTS - WINDOW 1510-1410 cm^{-1}

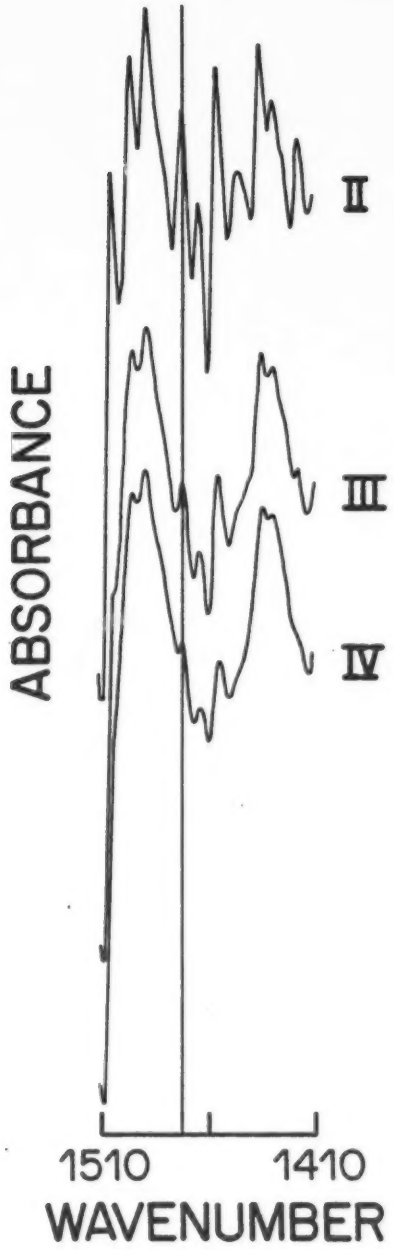


FIGURE 60

DRIFT ANALYSIS OF COAL-B
MOISTURE SATURATED AIR FLOW
EXPERIMENTS - WINDOW 1450-1150 cm^{-1}

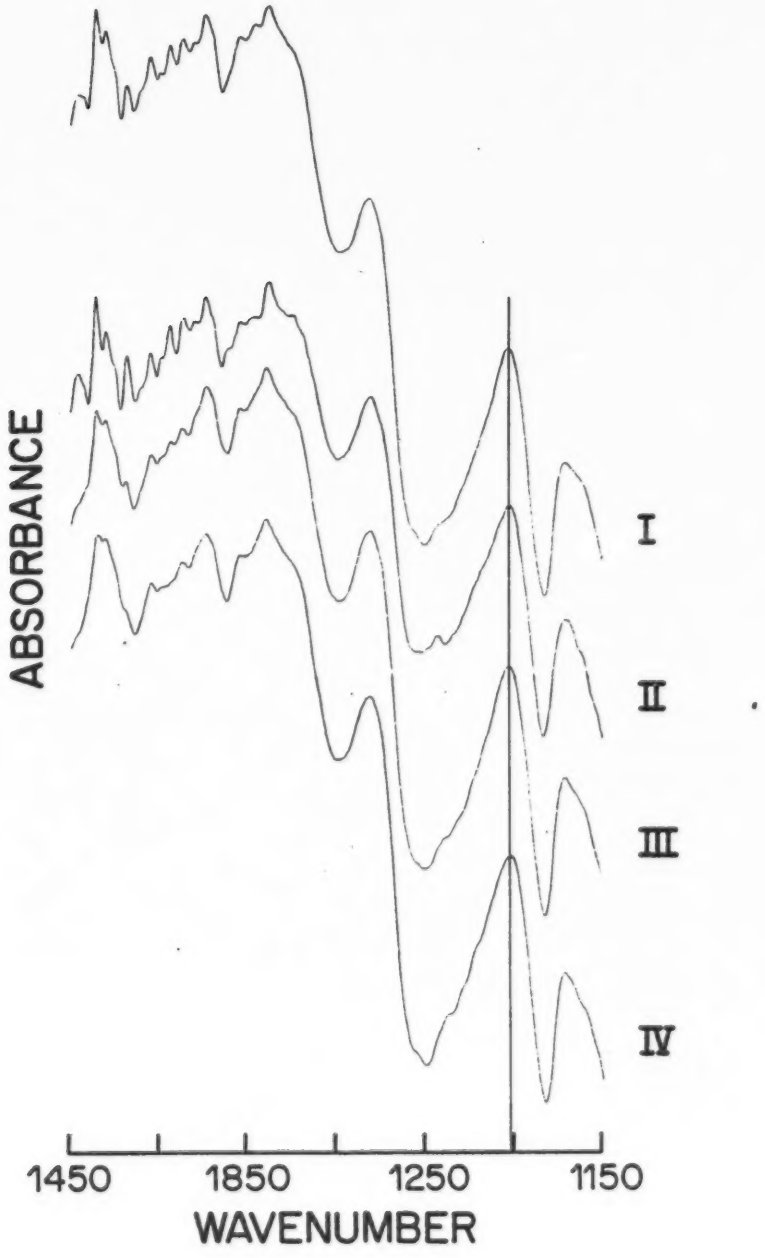


FIGURE 61

DRIFT ANALYSIS OF COAL-B
MOISTURE SATURATED AIR FLOW
EXPERIMENTS - WINDOW 1150-1000 cm^{-1}

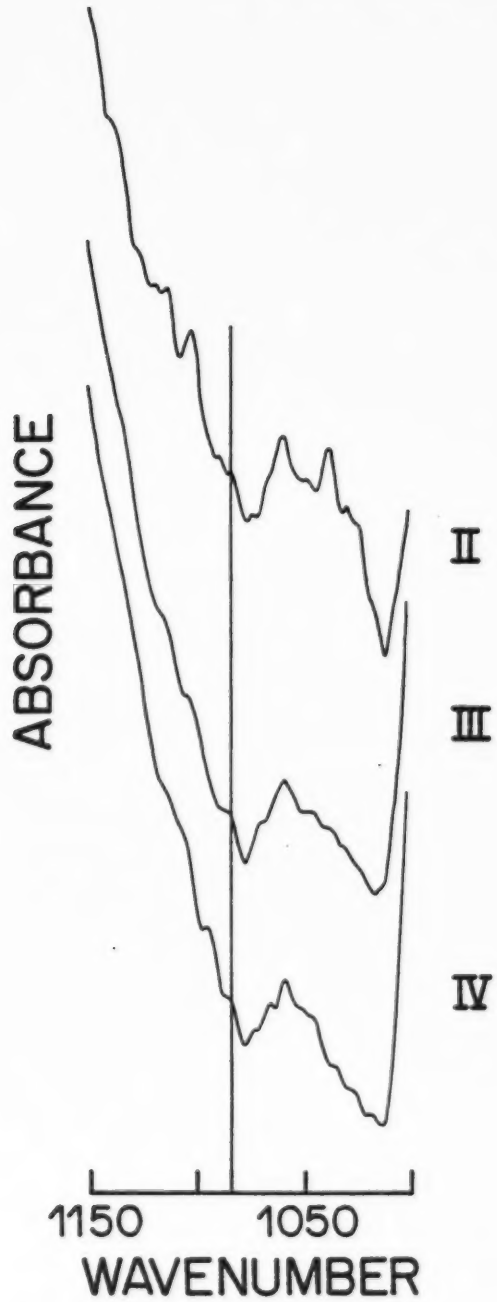


FIGURE 62

PEROXYGEN CONTENT VS EQUILIBRIUM MOISTURE

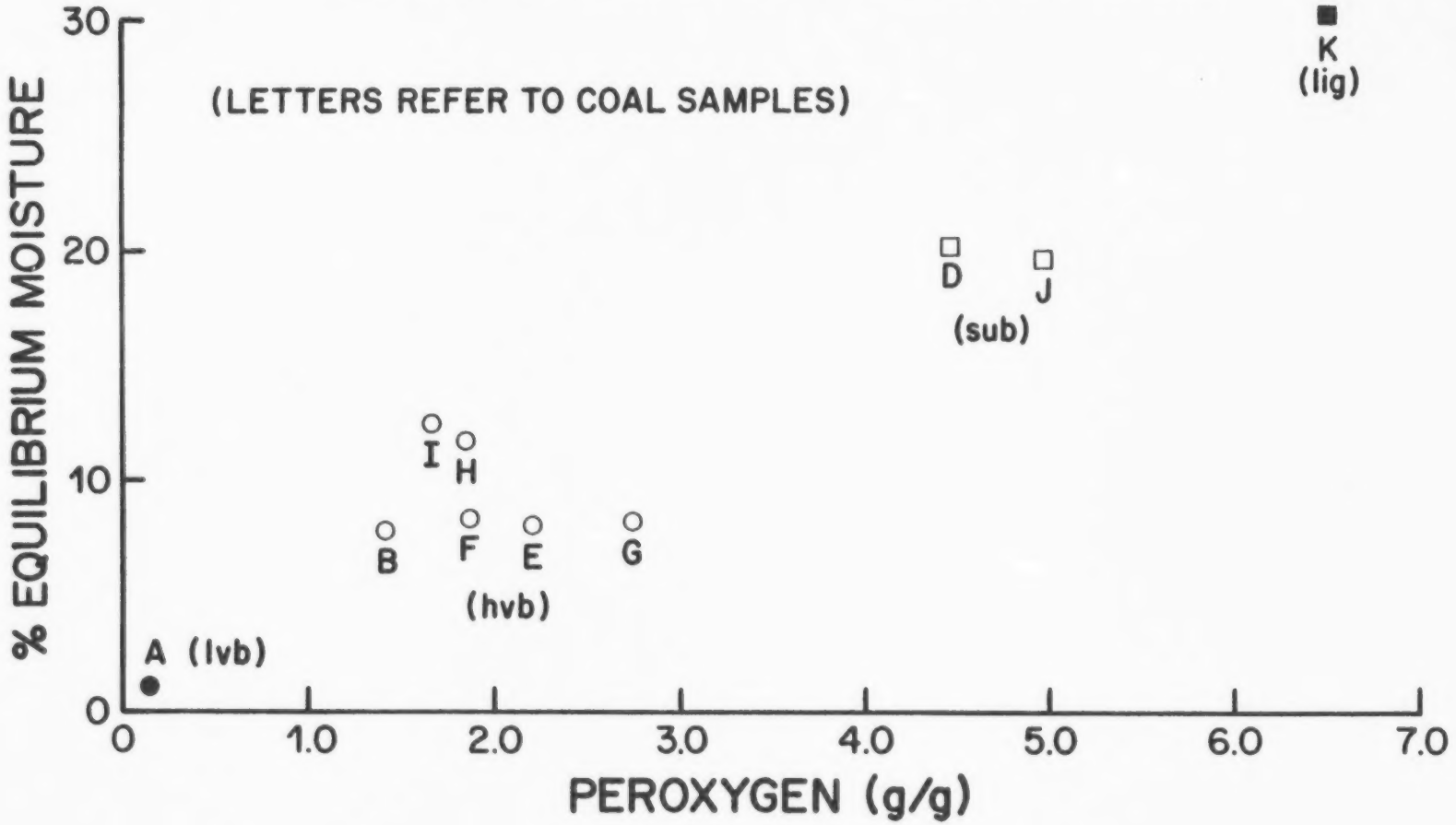


FIGURE 63

g VS %C AND %O

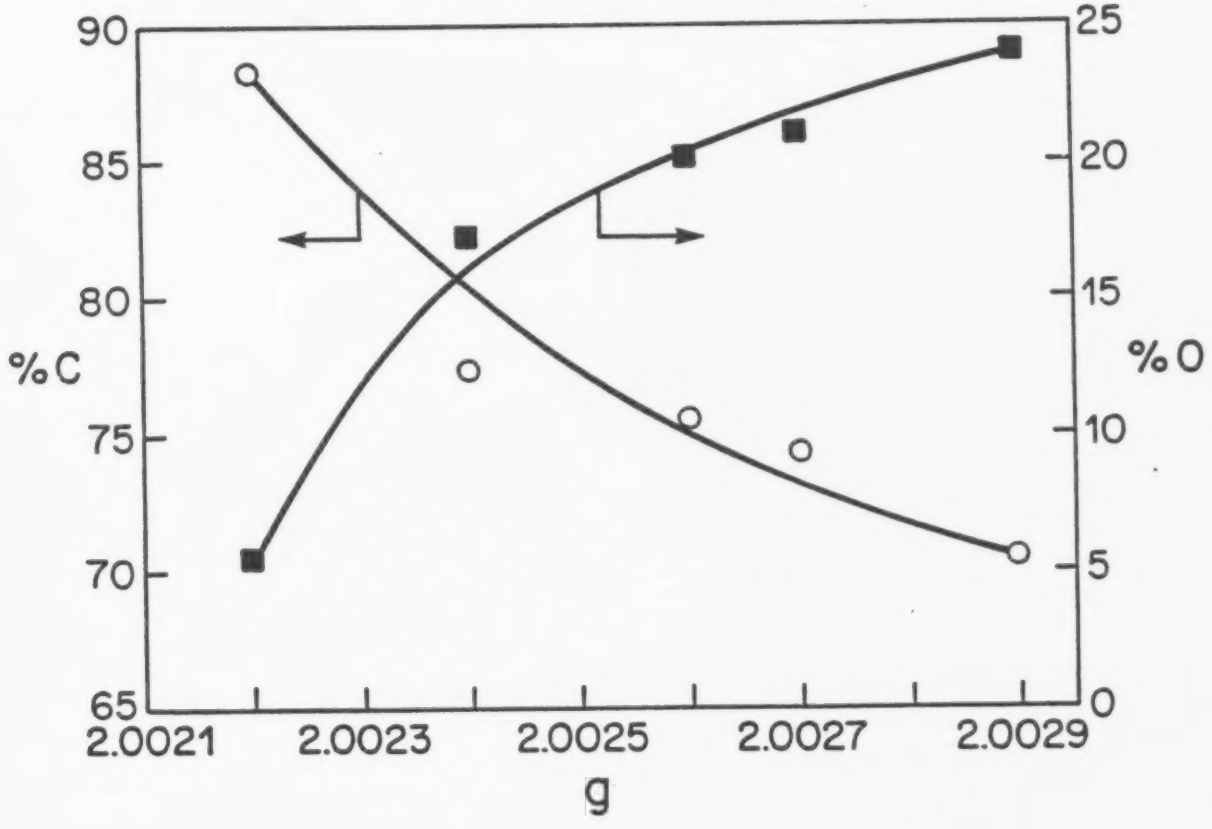


FIGURE 64

g VS HETEROATOM CONTENT ($\Sigma\xi X_n$)

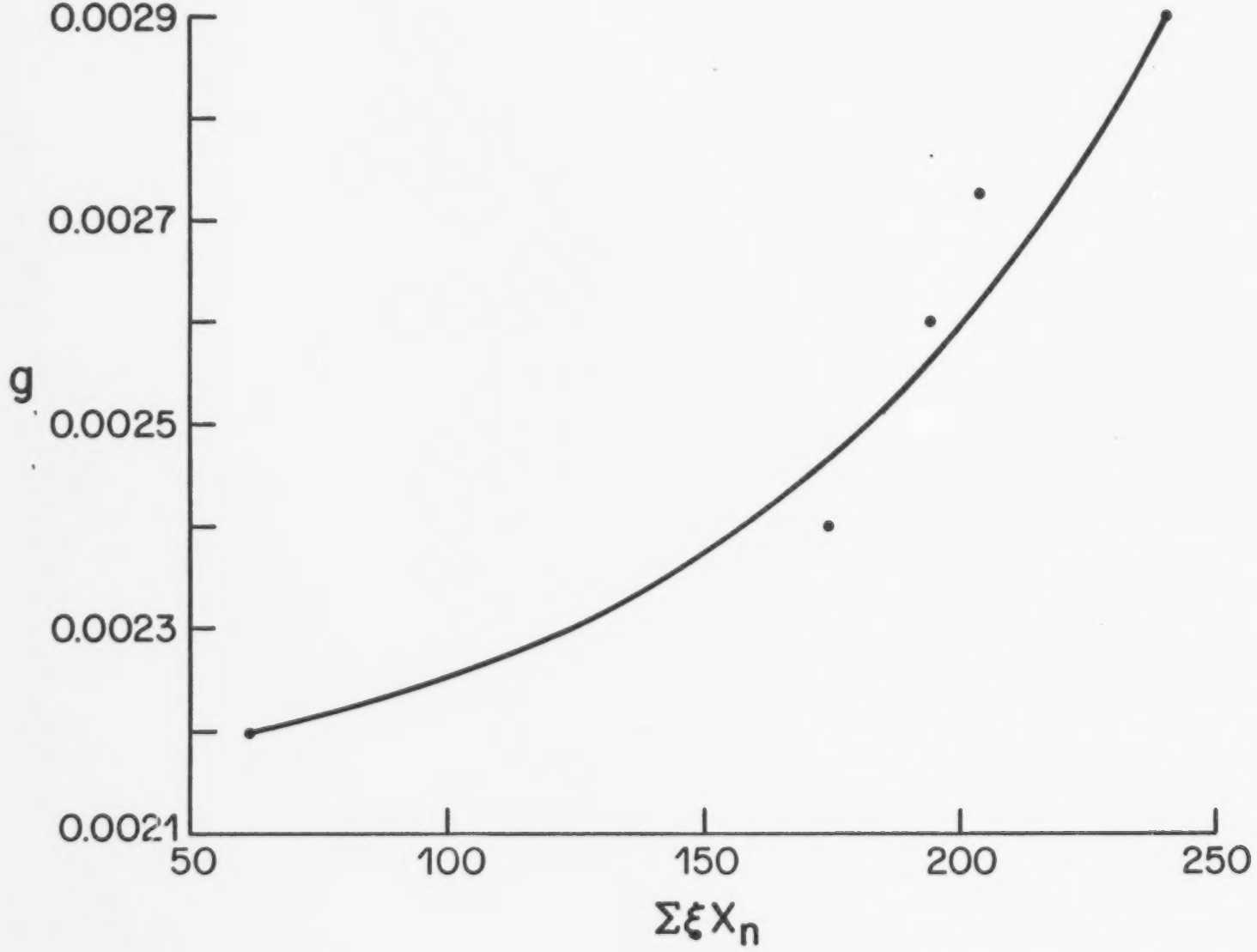
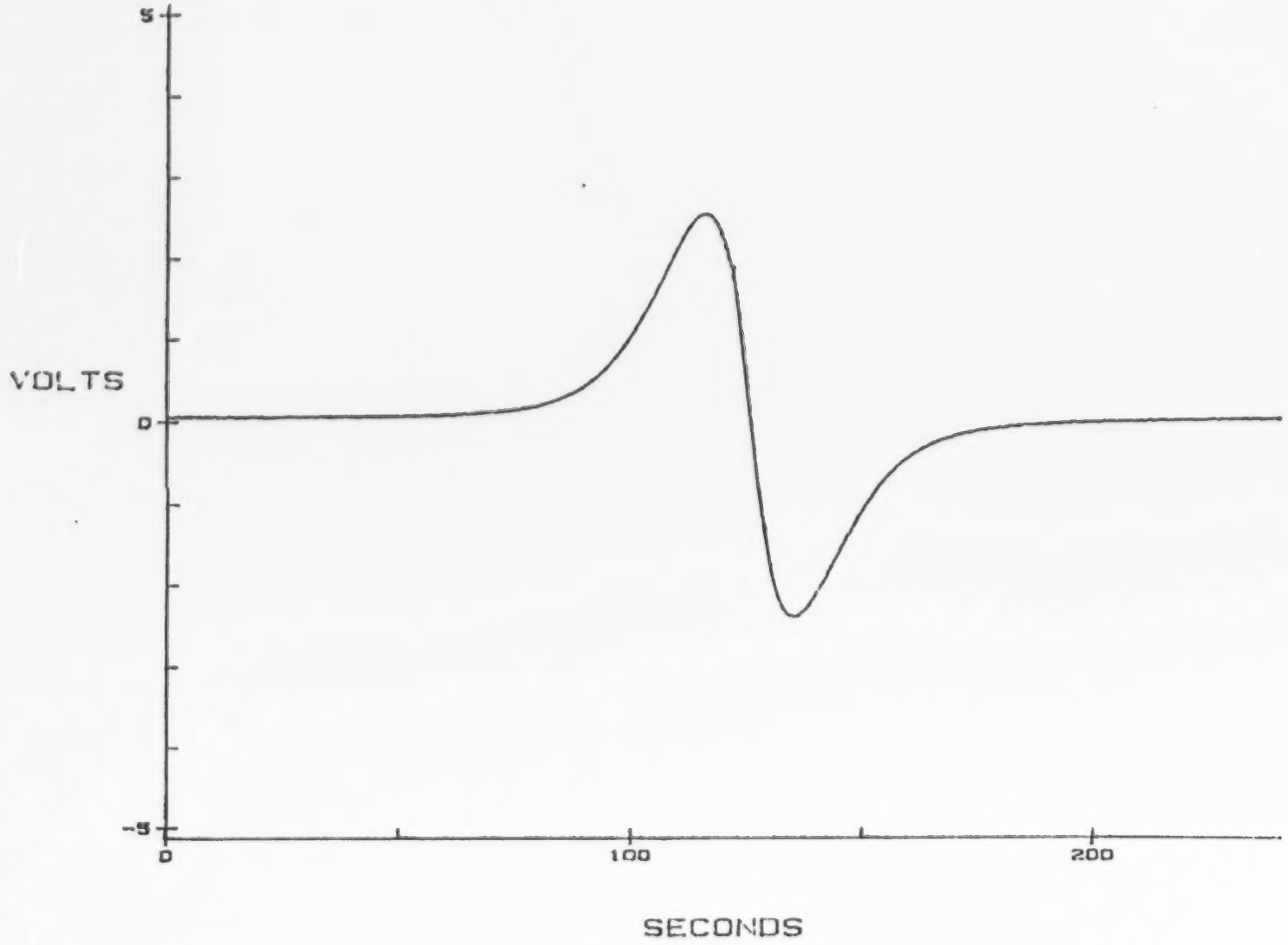


Figure 65. A typical E.P.R. Spectrum



Legend for Figures 66 (A-F)

Argand (DISPA) diagrams of Coal B: "Sequential gas flow Experiments"

A - Moisture equilibrated sample

B - Dried sample (Vacuum/P_2O_5)

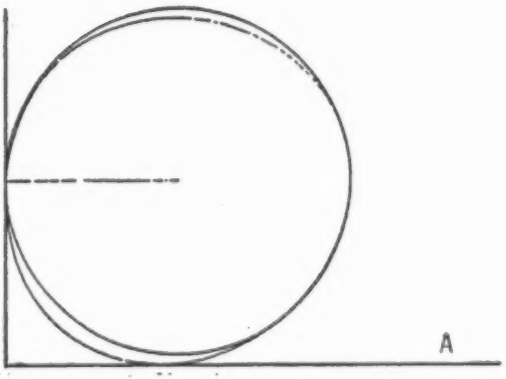
C - (B) treated with moist N_2

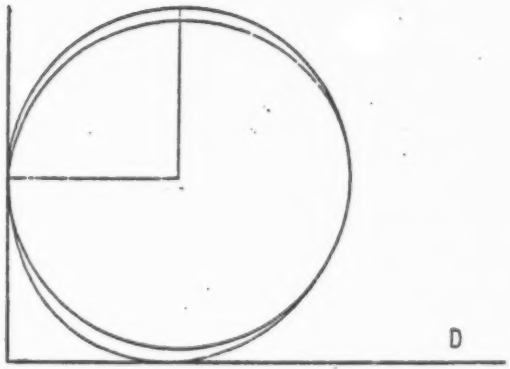
D - (C) redried (Vac/P_2O_5) and treated with moist N_2

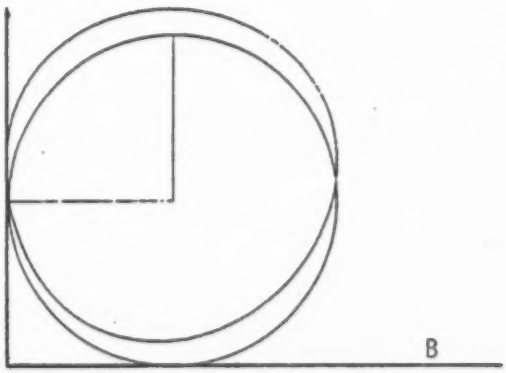
E - (D) redried (Vac/P_2O_5) and treated with moist air

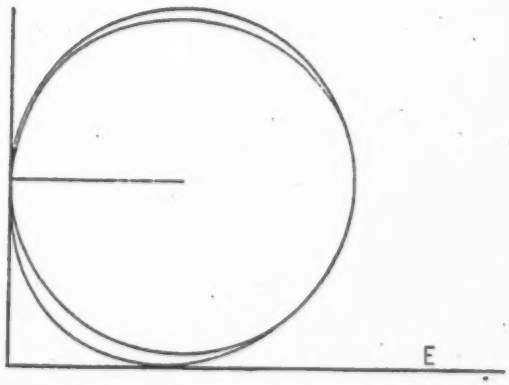
F - (B) treated with moist air

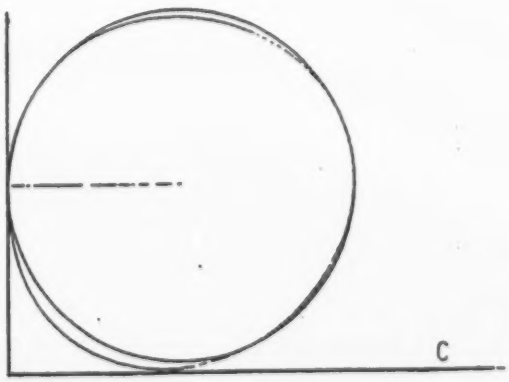
Figure 66 (A-F). Argand (DISPA) diagrams of Coal-B "Sequential gas flow experiments"

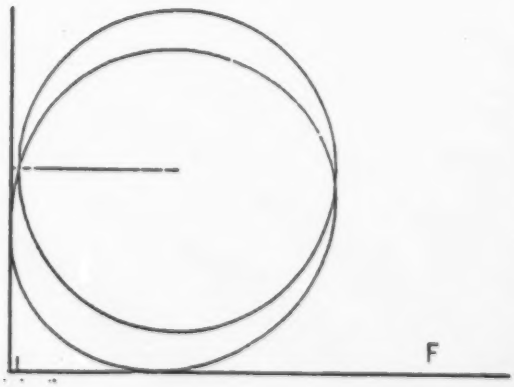












Legend for Figures 67 (A-F)

Argand (DISPA) diagrams of Coal C: "Sequential gas flow Experiments"

A - Moisture equilibrated sample

B - Dried sample (Vacuum/P_2O_5)

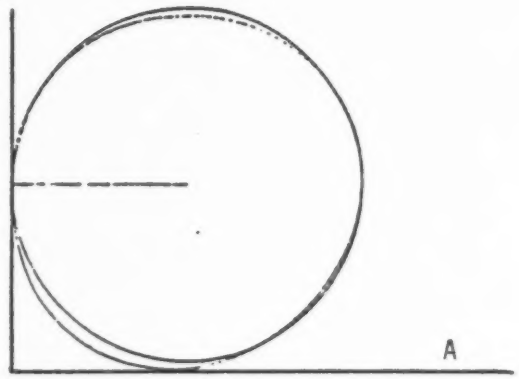
C - (B) treated with moist N_2

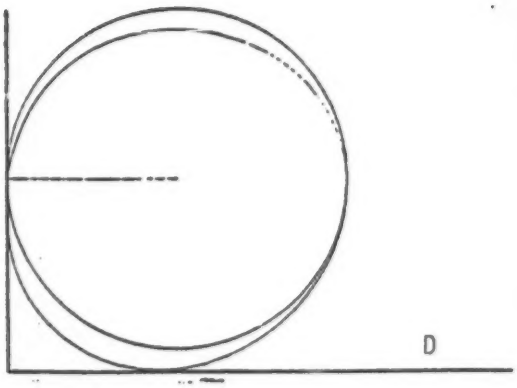
D - (C) redried (Vac/P_2O_5) and treated with moist N_2

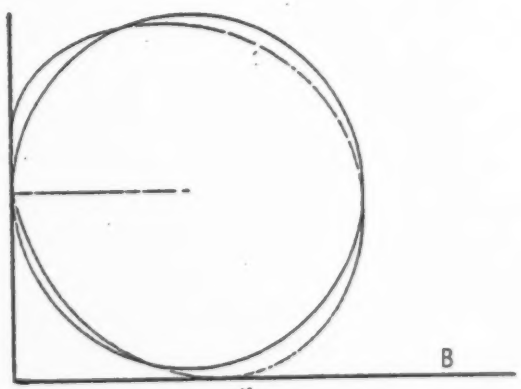
E - (D) redried (Vac/P_2O_5) and treated with moist air

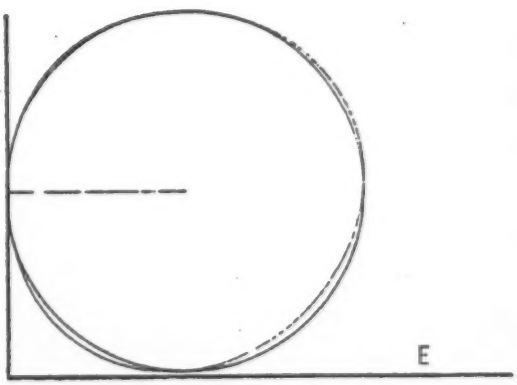
F - (B) treated with moist air

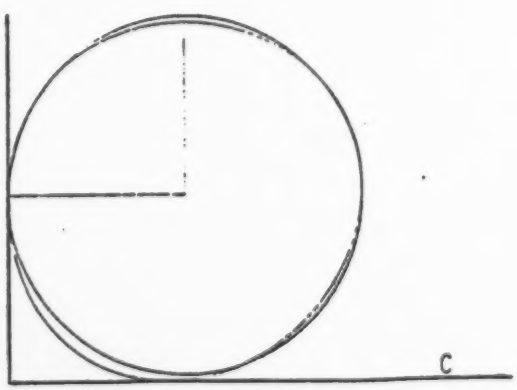
Figure 57 (A-F). Argand (DISPA) diagrams of Coal-C "Sequential gas flow experiments".

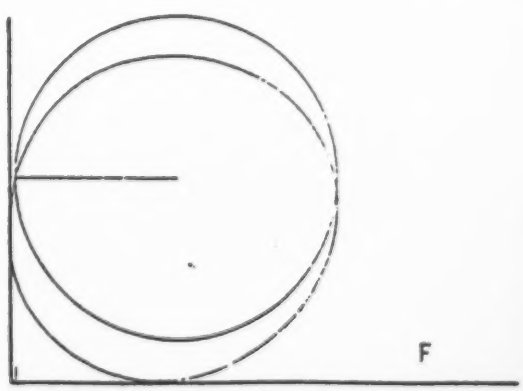












Legend for Figures 68 (A-F)

Argand (DISPA) diagrams of Coal D: "Sequential gas flow Experiments"

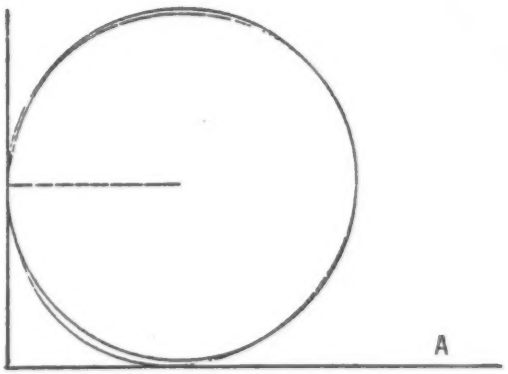
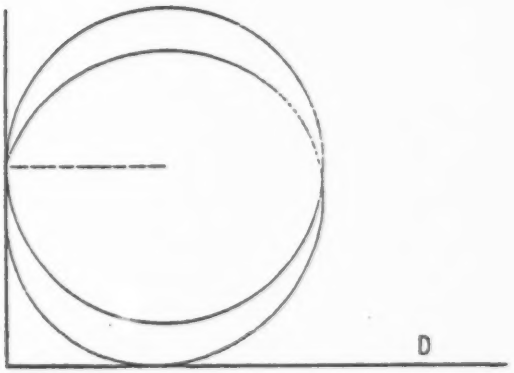
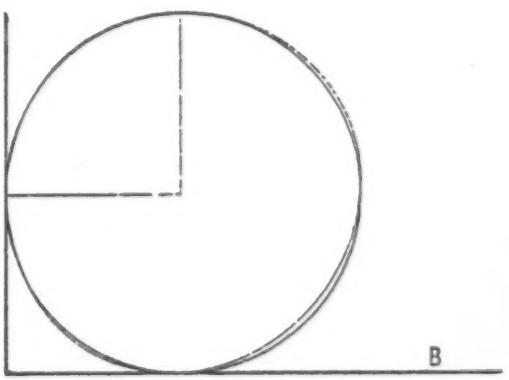
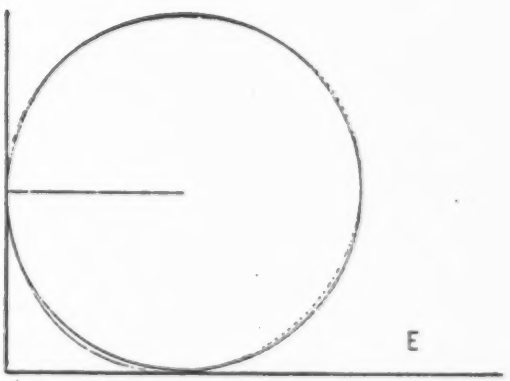
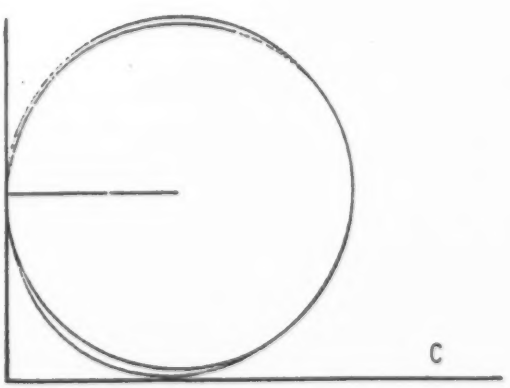
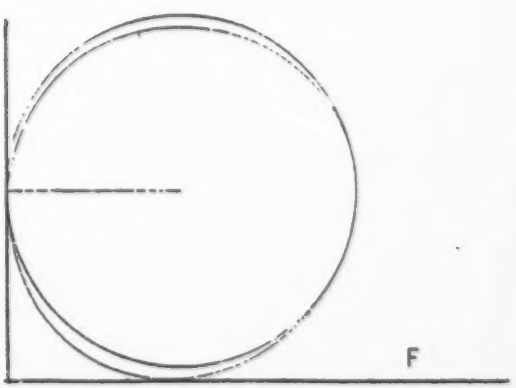
A - Moisture equilibrated sample

B - Dried sample (Vacuum/P_2O_5)

C - (B) treated with moist N_2

D - (C) redried (Vac/P_2O_5) and treated with moist N_2

E - (D) redried (Vac/P_2O_5) and treated with moist air

F - (B) treated with moist air

Figures 68 (A-F). Argand (DISPA) diagrams of Coal-D "Sequential gas flow experiments"